

PATENT SPECIFICATION

(11) 1 571 481

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- (21) Application No. 48498/75 (22) Filed 26 Nov. 1975
 (21) Application No. 25528/76 (22) Filed 19 June 1976
 (21) Application No. 39618/76 (22) Filed 23 Sept. 1976
 (23) Complete Specification filed 18 Nov. 1976
 (44) Complete Specification published 16 July 1980
 (51) INT CL³ C07D 249/08; A01N 43/64
 (52) Index at acceptance

C2C 1175 1450 200 215 220 221 225 226 22Y 246 247 250 252
 25Y 290 29Y 30Y 313 31Y 321 322 323 32Y 338 364
 36Y 620 634 662 670 680 682 699 69Y 729 776 77Y
 805 80Y AA LH NG ZL

A5E 239 247 249 251 252 262 269 270 273 275 278 279 500
 504 506 507 A

C1B 3F1

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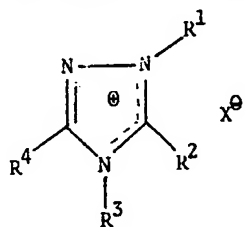


(54) 1,2,4-TRIAZOLIUM COMPOUNDS HAVING PESTICIDAL AND PLANT GROWTH REGULATING PROPERTIES

(71) We, FISON'S LIMITED, a British Company of Fison House, 9 Grosvenor Street, London W1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

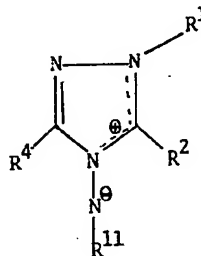
This invention relates to triazolium compounds.

The invention provides a method of combating pests at a locus infested or liable to be infested with them or of regulating the growth of a desired plant at a locus at which the plant is growing or is to grow, which method comprises applying to the locus a pest-combating or a plant growth regulant amount of a compound which is a 1,2,4-triazolium salt of formula



(I)

or

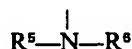


(II)

in which R¹ represents a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, aralkyl, or heterocyclic group;

R² and R⁴ are the same or different and each represents a hydrogen atom or a substituted or unsubstituted alkylthio, arylthio, or aralkylthio group or a group as defined for R¹;

R³ represents a group as defined for R¹ or the group



where R⁶ represents a hydrogen atom or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl or aryl group;

R⁵ represents a hydrogen atom; —SO₂R⁷ or



where A represents an oxygen or sulphur atom, Z represents a single bond, an oxygen or sulphur atom or an



- 5 group, R⁷ represents a substituted or unsubstituted alkyl, aryl or aralkyl group and R⁸ represents a hydrogen atom or a group as defined for R⁷; or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl or aryl group; 5
 or R⁸ and R⁹ together represent a group of formula =CR⁹R¹⁰ where R⁹ and R¹⁰ are the same or different and each represent a hydrogen atom or a substituted or 10
 10 unsubstituted alkyl, aryl or aralkyl group, or R⁹ and R¹⁰ together represent an alkylene chain; 10
 R¹¹ represents a group —SO₂R⁷ or



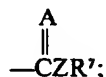
- wherein 15
 15 A, Z and R⁷ are as defined above, and
 X[⊖] represents one equivalent of an anion. 15
 The invention also provides a pesticidal or plant growth regulant composition comprising a compound of formula I or II together with at least one material selected from solid carriers, a liquid carrier which is a hydrocarbon which boils 20
 20 within the range 130—270°C, surface active agents, other pesticides, other plant-growth regulants, antidotes, ammonium sulphate, fertilizers and bases. 20
 Furthermore, the invention provides a new compound of formula II or of formula I where R³ represents the group



- 25 R¹ represents a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aralkyl, or heterocyclic group; 25
 R² and R⁴ are the same or different and each represents a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, aralkyl, alkylthio of more than one carbon atom, arylthio, aralkylthio or a heterocyclic 30
 30 group; with the proviso that R² and R⁴ do not both represent methyl; 30
 R⁵ represents a hydrogen atom; —SO₂R⁷ or



- or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl or aralkyl group; 35
 35 R⁶ represents a hydrogen atom or a substituted or unsubstituted alkyl or aralkyl group;
 or R⁵ and R⁶ together represent a group of formula =CR⁹R¹⁰; and R¹¹ represents a group —SO₂R⁷ or



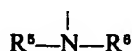
- 40 with the proviso that, when R¹ represents methyl, R² and R⁴ represent phenyl and X[⊖] represents bromide or iodide, then R³ does not represent amino. 40
 In a narrower group of these new compounds
 R¹ represents a substituted or unsubstituted alkyl or aralkyl group; and
 R² and R⁴ are the same or different and each represents a substituted or

unsubstituted alkyl, alkenyl, alkynyl, aryl, cycloalkyl or cycloalkenyl group; with the proviso that R^2 and R^4 do not both represent methyl.

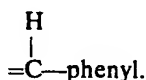
In this narrower group, in a particular embodiment, R^2 and R^4 are the same or different and each represents an aryl group which is unsubstituted or substituted.

In another narrower group R^5 and R^6 are preferably each hydrogen or optionally substituted, but preferably unsubstituted alkyl. Desirably at least one of R^5 and R^6 represents alkyl, preferably unsubstituted, e.g., R^5 represents a hydrogen atom and R^6 represents an alkyl group.

The invention also provides those compounds of formula I where R^3 represents the group



and X^\ominus represents alkyl sulphate with the exception of that compound of formula I where X^\ominus represents methyl sulphate, R^1 represents methyl, R^2 and R^4 each represent a hydrogen atom and R^5 and R^6 together represent



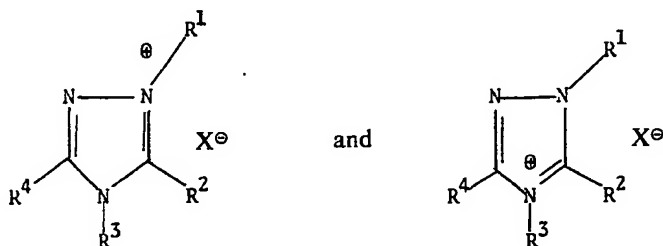
In a narrower group within these new compounds, R^1 represents a substituted or unsubstituted alkyl, aryl or aralkyl group; and

R^2 and R^4 are the same or different and each represents a hydrogen atom or a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, aralkyl or alkylthio group. In one embodiment within this narrower group R^2 and R^4 are the same or different and each represents a hydrogen atom or a substituted or unsubstituted alkyl, aryl, aralkyl or alkylthio group.

The invention also provides those compounds of formula I where R^1 represents a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aralkyl or heterocyclic group (preferably an optionally substituted, but especially an unsubstituted, alkyl group); R^3 represents a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, aralkyl or heterocyclic group (preferably an optionally substituted, but especially an unsubstituted, alkyl group); and R^2 and R^4 are the same or different and each represents a hydrogen atom or a substituted or unsubstituted alkylthio, arylthio or aralkylthio, group, or a group as defined for R^3 ; with the proviso that R^2 does not represent hydrogen or a substituted or unsubstituted alkyl or aryl group when R^1 represents a substituted or unsubstituted alkyl group R^4 represents a substituted or unsubstituted alkyl or aryl group and R^3 represents a substituted or unsubstituted alkyl group, and with the proviso that any phenyl group of the group R^4 is not substituted by $-NO_2$. Within these new compounds, there may be mentioned two important groups, namely those compounds wherein R^3 represents substituted or unsubstituted aryl or aralkyl, and those compounds wherein one or more of R^1 , R^2 , R^3 and R^4 represents substituted or unsubstituted alkenyl, alkynyl, cycloalkyl, cycloalkenyl or aromatic heterocyclyl.

The invention also provides processes for the preparation of the new compounds, which processes are those defined below for the production of the compounds in general but applied to the production of novel compounds.

The dotted line in formula I indicates that the structure of the compound lies between



For each set of meanings for the symbols, only a single compound has found to be involved, not two isomers. The dotted line in formula II is analogous.

It can be seen that the compound of formula II is an internal salt and that of formula I is an external salt, the compound of formula II being the corresponding internal salt, where possible, of the compound of formula I where R^3 represents

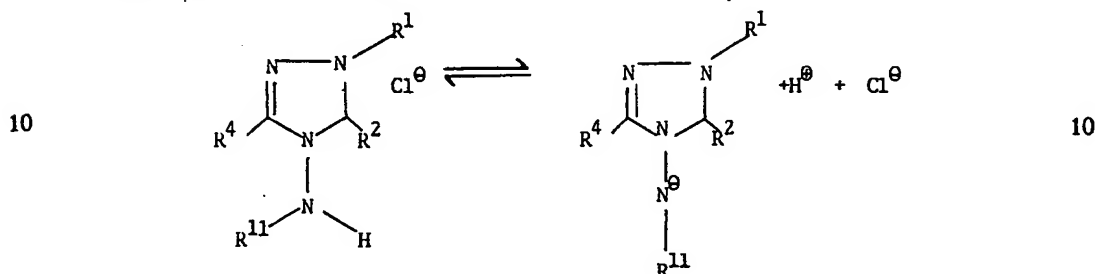


5 For internal salt formation, R^5 must represent a group $-SO_2R^7$ or



as defined hereinbefore, i.e. a group R^{11} .

In aqueous solution of such compounds of formula I an equilibrium exists with the compounds of formula II, e.g.



Such pairs of compounds are generally of analogous activity. Differences in solubility etc., of the two types may lead to a different degree of activity between the two types.

15 Similarly, since in the compounds of formula I it is the cation which is responsible for the activity e.g., on plant physiology, any anion can generally be employed and it may be chosen bearing other factors in mind such as convenience in manufacture of the cation. X^\ominus can for example represent Cl^\ominus , Br^\ominus , I^\ominus , NO_2^\ominus , $\frac{1}{2}SO_4^{\ominus\ominus}$, ClO_4^\ominus , $\frac{1}{2}PO_4^{\ominus\ominus\ominus}$, BF_4^\ominus , FSO_3^\ominus , CH_3COO^\ominus , OH^\ominus , $\frac{1}{2}CO_3^{\ominus\ominus}$, HCO_3^\ominus , Br_3^\ominus , I_3^\ominus , RSO_3^\ominus where R represents an alkyl, aryl, alkoxyaryl or alkylaryl group, or RSO_4^\ominus where R represents an alkyl group.

20 Multivalent anions such as sulphate and phosphate may have associated with them a cation in addition to the 1,2,4-triazolium cation, for example a proton or an alkali metal or alkaline earth metal. For simplicity, such anions can be depicted as being not further ionized though in fact they probably are further ionized. Examples are $NaSO_4^\ominus$, $KPO_4^{\ominus\ominus}$, $MgPO_4^\ominus$, HSO_4^\ominus and $NaHPO_4^\ominus$.

25 Generally preferred is X representing chlorine, bromide, iodide, acetate, hydroxide, sulphate, hydrogen sulphate, alkyl sulphate, *p*-toluene sulphonate, perchlorate or alkyl sulphonate. For convenience in manufacture when R^1 represents an alkyl group and X^\ominus represents alkyl sulphate, the alkyl group of the alkyl sulphate is preferably the same as R^1 , e.g. both methyl or both ethyl. Preferably, X^\ominus represents halide or alkyl sulphate, especially chloride, bromide, methyl sulphate or ethyl sulphate.

30 The internal salt of formula II may be prepared by reacting the external salt of formula I where R_3 represents $-NHR^5$, R^5 being a group $-SO_2R^7$ or



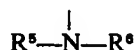
35 as defined hereinbefore, i.e. a group R^{11} , with a base, such as sodium hydroxide. The reaction is usually conducted in the presence of an inert solvent. The reaction may be conducted for example at a temperature of 0–50°C.

The external salt of formula I where R^3 represents

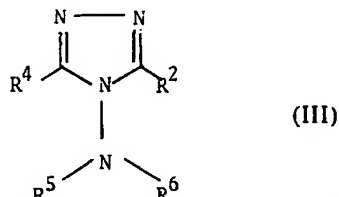


in which R^5 represents a group R^{11} , may be prepared by reacting an internal salt of formula II with a compound of formula R^6X . The reaction is usually conducted in an inert solvent and may be carried out at a temperature for instance of 0—200°C. When R^5 represents a hydrogen atom, an external salt of formula I is prepared which is a counterpart to the internal salt of formula II; but when R^6 represents other than hydrogen (e.g. when the compound of formula R^6X is dimethylsulphate) the external salt of formula I prepared has no counterpart of formula II.

The compounds of formula I where R^3 represents

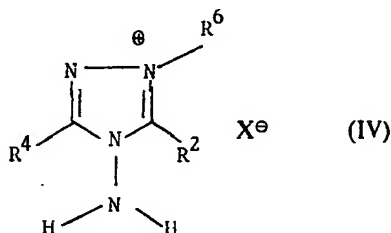


are preferably prepared by quaternising a 1,2,4-triazole of formula



with a compound of formula R^6X , wherein R^1 , R^2 , R^4 , R^5 , R^6 and X are as in formula I or II. The quaternisation may be carried out with or without an inert solvent. It may be conducted at a temperature for instance of 0—200°C.

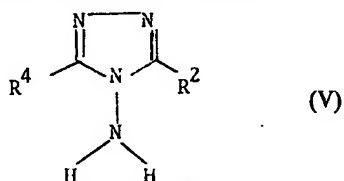
The 1,2,4-triazole of formula III where R^5 is hydrogen can be prepared by heating in the presence of a base, such as sodium hydroxide, a 4-amino-1,2,4-triazolium derivative of formula



wherein

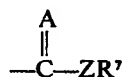
R^2 , R^4 , R^6 and X^\ominus are as in formula I or II. The reaction is usually conducted in the presence of an inert solvent, e.g. water, and may be carried out for example at a temperature of 50—150°C.

The 4-amino-1,2,4-triazolium derivative of formula IV can be prepared by quaternising a 4-amino-1,2,4-triazole derivative of formula



with a compound of formula R^6X , wherein R^2 , R^4 , R^6 and X are as in formula I or II. The quaternisation may be carried out with or without an inert solvent. It may be conducted at a temperature for instance of 0—200°C.

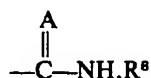
The compounds of formula III where R^5 represents $-\text{SO}_2R^7$ or



may be prepared by reacting the corresponding compound of formula III in which R^5 represents a hydrogen atom with a halide or anhydride of formula R^5Y or R^5OR^5 , where Y represents a halogen, usually chlorine, atom. The reaction is

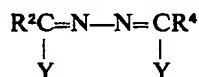
usually conducted in the presence of an inert solvent and may be carried out at a temperature of for example 50—150°C.

The compound of formula III in which R⁵ represents



5 may be prepared by reacting the corresponding compound in which R⁵ represents a 5
hydrogen atom with an isocyanate or isothiocyanate of formula R⁶NCO or R⁶NCS
respectively. The reaction is usually conducted at a temperature of 0 to 150°C, for
example at ambient temperature, in an organic solvent, e.g. dimethylformamide,
10 dimethyl sulphoxide, acetonitrile or a hydrocarbon (e.g. toluene), and preferably, 10
when A represents a sulphur atom, also in the presence of a catalyst (usually a
tertiary amine, e.g. triethylamine or pyridine, or an organotin compound, e.g.
dibutyltin diacetate).

15 The compounds of formula III where R⁵ and R⁶ both represent substituted or 15
unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aryl or aralkyl groups or together
represent a group =CR⁹R¹⁰ may be prepared by reacting a compound of formula

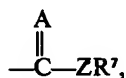


with a hydrazine compound of the formula R⁵R⁶NNH₂.

20 Where R⁵ and R⁶ represent a group =CR⁹R¹⁰, the compound of formula III 20
may be reduced using for example sodium borohydride to give a further compound
of formula III where R⁵ represents hydrogen and R⁶ represents the group
—CHR⁹R¹⁰.

25 The compound of formula I in which R⁵ and R⁶ together represent a group of 25
formula =CR⁹R¹⁰ may be prepared by reacting the corresponding compound in
which R⁵ and R⁶ each represent a hydrogen atom with an aldehyde or ketone of
formula R⁶COR¹⁰ wherein R⁶ and R¹⁰ are as in formula I. The reaction is usually
conducted in the presence of an inert solvent and may be carried out at a
temperature for example of 50—200°C. Alternatively, a compound of formula V
may be reacted with a compound of formula R⁶COR¹⁰, and the product
subsequently quaternised.

30 The compound of formula I in which R⁵ represents —SO₂R⁷ or 30



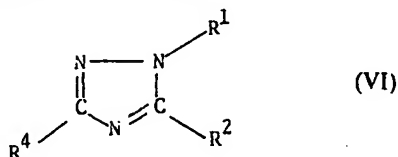
35 i.e. a group R¹¹, may be prepared by reacting the corresponding compound of 35
formula I or II in which R⁵ represents a hydrogen atom with a halide or anhydride
of formula R⁵Y or R⁵OR⁵. The reaction is usually conducted in the presence of an
inert solvent and may be carried out at a temperature of for example 50—150°C. If
excess base is present, the compound of formula I produced can be converted
directly to a compound of formula II.

The compound of formula I in which R⁵ represents



40 may be prepared by reacting the corresponding compound in which R⁵ represents a 40
hydrogen atom with an isocyanate or isothiocyanate of formula R⁶NCO or R⁶NCS
respectively. The reaction is usually conducted at a temperature of 0 to 150°C, for
example at ambient temperature, in an organic solvent, e.g. dimethylformamide,
45 dimethyl sulphoxide, acetonitrile or a hydrocarbon (e.g. toluene), and preferably, 45
when A represents a sulphur atom, also in the presence of a catalyst (usually a
tertiary amine, e.g. triethylamine or pyridine, or an organotin compound, e.g.
dibutyltin diacetate).

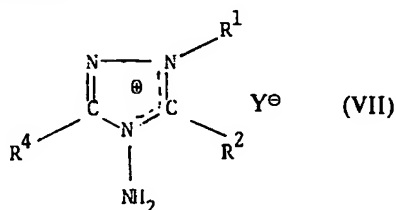
The compounds of formula I where R^3 represents a group as defined for R^1 may be prepared by reacting a triazole of formula



wherein

R^1 , R^2 and R^4 are as in formula I or II, with a compound of formula R^3X where X is as defined in formula I and R^3 is as defined for R^1 in formula I. The reaction is conveniently effected by heating.

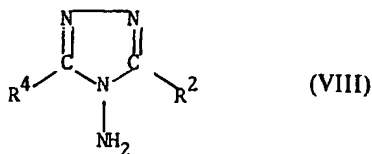
The compounds of formula VI may be prepared by reacting a 4-aminotriazolium salt of the formula



wherein

R^1 , R^2 and R^4 are as in formula I or II, and Y^\ominus represents one equivalent of an anion, with nitrous acid. The nitrous acid is desirably generated *in situ* in a manner known *per se*, e.g. by reaction between an alkali-metal nitrite (e.g. sodium nitrite) and a mineral acid (e.g. hydrochloric acid) with cooling.

The compounds of formula VII may be prepared from the corresponding compounds of the formula

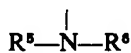


wherein

R^2 and R^4 are as in formula I or II, with a compound of formula R^1Y wherein R^1 is as in formula I or II and Y is as defined above. The reaction is conveniently effected by heating.

The present processes may be conducted for example at a pressure of 0.5 to 10, preferably 1—1.1, atmospheres.

In a preferred embodiment, a novel compound as defined above and having formula I where R^1 represents an alkyl group (preferably C 1 to 6 alkyl, e.g. methyl or ethyl) and R^3 represents



is prepared by quaternising the corresponding 1,2,4-triazole of formula III with a compound of formula R^1X (e.g. dimethyl or diethyl sulphate, or methyl or ethyl bromide) where X represents alkyl sulphate, (e.g. methyl sulphate or ethyl sulphate) or bromide in which the alkyl group is R^1 (e.g. methyl or ethyl).

In one aspect, the present compounds are of formula II or are of formula I where R^3 represents the group



A preferred group within this aspect are those wherein

R^1 represents a substituted or unsubstituted alkyl, aryl or aralkyl group; and

R^2 and R^4 are the same or different and each represents a hydrogen atom or a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl,

aralkyl or alkylthio group. Within this group, in one embodiment, R^2 and R^4 are the same or different and each represents a hydrogen atom or a substituted or unsubstituted alkyl, aryl, aralkyl or alkylthio group.

5 In a particular embodiment within this aspect, R^2 and R^4 are the same or different and each represents a hydrogen atom or an alkyl, aryl, aralkyl or alkylthio group which is unsubstituted or substituted. 5

10 In the other aspect, the present compounds are of formula I where R^3 represents a group as defined for R^1 . In a preferred group within this aspect, R^1 and R^3 are the same or different and each represents a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, aralkyl or aromatic heterocyclyl group. 10

15 When R^1 , R^2 , R^3 or R^4 represents a substituted group, the substituent(s) may be for example one or more substituents selected from halogen, alkoxy, alkylthio, alkylsulphonyl, alkylsulphinyl, acyl, nitro, cyano, carboxy, esterified, salified or amidated carboxy (e.g. alkoxycarbonyl), amine, substituted (e.g. by 1 or 2 alkyl groups) amino and, except when it represents substituted alkyl, alkyl. When R^5 or R^6 represents a substituted alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl or aryl group or R^9 or R^{10} represents a substituted alkyl, aralkyl or aryl group, the substituent(s) may be for example one or more selected from halogen, alkoxy and nitro and, when R^5 , R^6 , R^9 or R^{10} represents a substituted aryl group, alkyl. Any substituted aryl group may for example be *m*-tolyl or *p*-tolyl. Examples of preferred substituent groups are fluorine, bromine, chlorine, methoxy, ethoxy, methylthio, ethylthio, methylsulphinyl and methylsulphonyl. 15

20 When any of the present symbols represents a substituted aralkyl group, the substituent(s) are usually on the aryl part of the group. 20

25 When any of the present symbols represents a substituted or unsubstituted group, it is preferably unsubstituted. When it is substituted, the substituents are usually the same, e.g. all chlorine or all methyl, and preferably any such substituted group is monosubstituted. 25

30 Any alkyl group involved in the present symbols is preferably of 1—15, e.g. 1—10, especially 1—6, carbon atoms, for example methyl, ethyl, propyl, isopropyl, butyl or hexyl. Any alkenyl or alkynyl group is preferably of 2—6 carbon atoms, for example vinyl or ethynyl or especially allyl or propargyl. Any cycloalkyl group is preferably of 3—7 carbon atoms, especially cyclohexyl or cyclopentyl. Any cycloalkenyl group is preferably of 3—7 carbon atoms, for example cyclopentenyl or especially cyclohexenyl. Any aryl group is preferably phenyl. Any aralkyl group is preferably phenylalkyl e.g. of 7—10 carbon atoms, especially benzyl. Any halogen is preferably fluorine, chlorine or bromine especially chlorine. Any acyl group is preferably alkanoyl of 1—7, e.g. 2—7, carbon atoms, e.g. formyl, acetyl or isobutyryl. 30

35 When any of R^1 , R^2 , R^3 and R^4 represents a substituted or unsubstituted heterocyclyl group, it is preferably a monocyclic group, and preferably contains oxygen, nitrogen or sulphur as sole hetero ring element. Preferred such groups are furyl, pyranyl, pyrrolyl, pyridyl, quaternised pyridyl and thienyl. 35

40 Thus, preferably, R^1 represents an alkyl of 1—6 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, cycloalkenyl of 3—7 carbon atoms, phenyl, phenylalkyl of 7—10 carbon atoms, furyl, pyranyl, pyrrolyl, pyridyl, quaternised pyridyl, or thienyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, hydroxy, mercapto, alkoxy of 1—6 carbon atoms, alkylthio of 1—6 carbon atoms, alkylsulphonyl of 1—6 carbon atoms, alkylsulphinyl of 1—6 carbon atoms, alkanoyl of 1—7 carbon atoms, nitro, cyano, carboxy, esterified, salified or amidated carboxy, amino, amino substituted by 1 or 2 alkyl groups of 1—6 carbon atoms, and, except where R^1 represents substituted alkyl, alkyl of 1—6 carbon atoms; 40

45 R^2 and R^4 are the same or different and each represents a hydrogen atom or an alkyl of 1—15 carbon atoms, alkylthio of 1—15 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, phenyl, phenylthio, phenylalkyl of 7—10 carbon atoms, phenylalkylthio of 7—10 carbon atoms, furyl, pyranyl, pyrrolyl, pyridyl, quaternised pyridyl, or thienyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, hydroxy, mercapto, alkoxy of 1—6 carbon atoms, alkylthio of 1—6 carbon atoms, alkylsulphonyl of 1—6 carbon atoms, alkylsulphinyl of 1—6 carbon atoms, alkanoyl of 1—7 carbon atoms, nitro, cyano, carboxy, esterified, salified or amidated carboxy, amino, amino substituted by 1 or 2 alkyl groups of 1—15 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, 45

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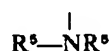
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cycloalkyl of 3—7 carbon atoms and, except when it represents substituted alkyl, alkyl of 1—6 carbon atoms;

R³ represents a group as defined for R¹ or the group



5 where R⁶ represents a hydrogen atom or an alkyl of 1—15 carbon atoms, alkenyl or
alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, phenylalkyl of
7—10 carbon atoms or phenyl group, which group is unsubstituted or substituted
by one or more substituents selected from halogen, alkoxy of 1—6 carbon atoms,
10 nitro and, except when R⁶ represents a substituted alkyl group, alkyl of 1—6 carbon
atoms;

R⁶ represents a hydrogen atom; —SO₂R⁷ or



where A represents an oxygen or sulphur atom, Z represents a single bond, an
oxygen or sulphur atom or an

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group, R⁷ represents alkyl of 1—6 carbon atoms, phenyl or phenylalkyl of 7—10
carbon atoms and R⁸ represents a hydrogen atom or a group as defined for R⁷; or
an alkyl of 1—6 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6
carbon atoms, cycloalkyl of 3—7 carbon atoms, phenylalkyl of 7—10 carbon
atoms or phenyl group, which group is unsubstituted or substituted by one or
more substituents selected from halogen, alkoxy of 1—6 carbon atoms, nitro
and, except when R⁸ represents a substituted alkyl group, alkyl of 1—6 carbon
atoms;

25

or R⁹ or R⁸ together represent a group of formula =CR⁹R¹⁰ where R⁹ and R¹⁰
are the same or different and each represent a hydrogen atom or an alkyl of 1—6
carbon atoms, phenyl or phenylalkyl of 7—10 carbon atoms group, which group is
unsubstituted or substituted by one or more substituents selected from halogen,
alkoxy of 1—6 carbon atoms, nitro and, except when it represents a substituted
alkyl group, alkyl of 1—6 carbon atoms, or together represents an alkylene chain of
30 3—7 carbon atoms,

and R¹¹ represents a group —SO₂R⁷ or



30

as defined immediately above.

35

In a preferred embodiment R¹ represents an alkyl of 1—10 carbon atoms,
phenyl or phenylalkyl of 7—10 carbon atoms group, which group is unsubstituted
or substituted by one or more substituents selected from halogen, alkoxy of 1—6
carbon atoms, alkylthio of 1—6 carbon atoms, alkylsulphonyl of 1—6 carbon
atoms, alkylsulphinyl of 1—6 carbon atoms, alkanoyl of 1—7, e.g. 2—7 carbon
atoms, nitro and, except where R¹ represents substituted alkyl, alkyl of 1—6 carbon
atoms;

40

R² and R⁴ are the same or different and each represent a hydrogen atom or an
alkyl of 1—10 (e.g. 1—6) carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of
2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, cycloalkenyl of 3—7 carbon
atoms, phenyl, phenylalkyl of 7—10 carbon atoms or alkylthio of 1—6 carbon
atoms group, which group is unsubstituted or substituted by one or more
substituents selected from halogen, alkoxy of 1—6 carbon atoms, alkylthio of 1—6
carbon atoms, alkylsulphinyl of 1—6 carbon atoms, alkylsulphonyl of 1—6 carbon
atoms, alkanoyl of 1—7, e.g. 2—7, carbon atoms, nitro and, except when it
represents substituted alkyl, alkyl of 1—6 carbon atoms;

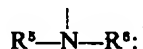
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R³ represents



R⁵ represents a hydrogen atom, —SO₂R⁷ or



5 where A represents an oxygen or sulphur atom, Z represents a single bond, an oxygen or sulphur atom, or an



10 group, R⁷ represents alkyl of 1—6 carbon atoms, phenyl or phenylalkyl of 7—10 carbon atoms and R⁸ represents a hydrogen atom or a group as defined for R⁷; or an alkyl of 1—6 carbon atoms, phenylalkyl of 7—10 carbon atoms or phenyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, alkoxy of 1—6 carbon atoms, nitro and, except when R⁸ represents a substituted alkyl group, alkyl of 1—6 carbon atoms;

15 R⁸ represents a hydrogen atom or an alkyl of 1—6 carbon atoms, phenylalkyl of 7—10 carbon atoms or phenyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, alkoxy of 1—6 carbon atoms, nitro and, except when R⁸ represents a substituted alkyl group, alkyl of 1—6 carbon atoms;

20 or R⁸ and R⁸ together represent a group of formula =CR⁹R¹⁰ in which R⁹ and R¹⁰ are the same or different and each represent a hydrogen atom or an alkyl of 1—6 carbon atoms, phenyl or phenylalkyl of 7—10 carbon atoms group, which group is unsubstituted or substituted by one or more substituents selected from halogen, alkoxy of 1—6 carbon atoms, nitro and, except when it represents a substituted alkyl group, alkyl of 1—6 carbon atoms, and

25 R¹¹ represents a group —SO₂R⁷ or



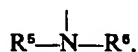
as defined immediately above.

30 A preferred group of novel compounds similarly have these preferred meanings of the symbols insofar as they fall within the definition of novel compounds above.

Preferably R² and R⁴ are the same.

Particular meanings of the symbols are given in the Examples.

35 Particularly preferred compounds are those of formula I or II in which R¹ represents alkyl, R² and R⁴ each represent aryl, each represent alkyl or each represent aryl monosubstituted by alkyl, R³ represents



R⁵ represents a hydrogen atom or alkyl and R⁶ represents alkyl.

The external salts of formula I are preferred.

Specific compounds which may be mentioned include the salts of the cations:

40 1,4-dimethyl-3,5-diphenyl-1,2,4-triazolium
1,4-dimethyl-3,5-di(p-tolyl)-1,2,4-triazolium
3,5-di(p-chlorophenyl)-1-ethyl-4-methyl-1,2,4-triazolium
1-ethyl-4-methyl-3,5-diphenyl-1,2,4-triazolium
45 1,4-dimethyl-3,5-di(m-tolyl)-1,2,4-triazolium
1-methyl-4-ethyl-3,5-di(m-tolyl)-1,2,4-triazolium
1,3-diphenyl-4,5-diethyl-1,2,4-triazolium
1,3-diphenyl-5-ethyl-4-methyl-1,2,4-triazolium, and
1,3-diphenyl-4,5-dimethyl-1,2,4-triazolium

1,4-dimethyl-3,5-di-*n*-pentyl-1,2,4-triazolium
1-methyl-3,5-di-*n*-pentyl-4-ethyl-1,2,4-triazolium,
especially the chlorides, bromides, methyl sulphates and ethyl sulphates thereof.

Specific preferred compounds include

- | | | |
|----|---|----|
| 5 | 4-amino-1-methyl-3,5-diphenyl-1,2,4-triazolium,
4-methylamino-1-methyl-3,5-diphenyl-1,2,4-triazolium,
4-methylamino-1-methyl-3,5-di(3-methylphenyl)-1,2,4-triazolium,
4-methylamino-1-ethyl-3,5-di(3-methylphenyl)-1,2,4-triazolium,
a mixture of 4-methylamino-1-ethyl-3-phenyl-5- <i>n</i> -pentyl-1,2,4-triazolium and 4- | 5 |
| 10 | methylamino-1-ethyl-3- <i>n</i> -pentyl-5-phenyl-1,2,4-triazolium,
4-amino-1- <i>n</i> -hexyl-1,2,4-triazolium,
4-amino-1- <i>n</i> -decyl-3,5-dimethyl-1,2,4-triazolium,
4- <i>n</i> -pentylamino-1- <i>n</i> -pentyl-3,5-dimethyl-1,2,4-triazolium,
4- <i>n</i> -pentylamino-1-(3-methylbutyl)-3,5-dimethyl-1,2,4-triazolium,
4- <i>n</i> -hexylamino-1- <i>n</i> -pentyl-3,5-dimethyl-1,2,4-triazolium,
4-amino-1- <i>n</i> -nonyl-3,5-diethyl-1,2,4-triazolium,
4-amino-1- <i>n</i> -decyl-3,5-diethyl-1,2,4-triazolium,
4-methylamino-1-methyl-3,5-di- <i>n</i> -butyl-1,2,4-triazolium,
4-ethylamino-1- <i>n</i> -pentyl-3,5-di- <i>n</i> -butyl-1,2,4-triazolium,
4-amino-1-(3-methylbutyl)-3,5-di- <i>n</i> -pentyl-1,2,4-triazolium,
4-methylamino-1-methyl-3,5-di- <i>n</i> -pentyl-1,2,4-triazolium,
4-ethylamino-1-methyl-3,5-di- <i>n</i> -pentyl-1,2,4-triazolium,
4-amino-1-methyl-3,5-di-(3-methylbutyl)-1,2,4-triazolium,
4-amino-1-ethyl-3,5-di-(3-methylbutyl)-1,2,4-triazolium,
4-methylamino-1-methyl-3,5-di-cyclopentyl-1,2,4-triazolium,
4-amino-1-methyl-3,5-di- <i>n</i> -octyl-1,2,4-triazolium,
4-methylamino-1-ethyl-3,5-di-cyclopentyl-1,2,4-triazolium,
4-amino-1-methyl-3,5-di- <i>n</i> -hexyl-1,2,4-triazolium,
4-amino-1-ethyl-3,5-di- <i>n</i> -hexyl-1,2,4-triazolium,
4-amino-1-ethyl-3,5-di- <i>n</i> -octyl-1,2,4-triazolium,
4-methylamino-1-methyl-3,5-di- <i>n</i> -octyl-1,2,4-triazolium,
4-methylamino-1-ethyl-3,5-di- <i>n</i> -octyl-1,2,4-triazolium,
4-methylamino-1-methyl-3,5-dicyclohexyl-1,2,4-triazolium, and
4-amino-1-methyl-3,5-di-(<i>p</i> -tolyl)-1,2,4-triazolium, salts
especially the chlorides or bromides and the methylsulphates of the 1-methyl
compounds, and the ethylsulphates of the 1-ethyl compounds. | 10 |
| 15 | Especially preferred are the
4-methylamino-1-ethyl-3,5-diphenyl-1,2,4-triazolium,
4-methylamino-1-ethyl-3,5-di(3-methylbutyl)-1,2,4-triazolium,
4-amino-1-methyl-3,5-di(3-methylbutyl)-1,2,4-triazolium,
4-amino-1-methyl-3,5-dipentyl-1,2,4-triazolium,
4-methylamino-1-methyl-3,5-dipentyl-1,2,4-triazolium,
4-methylamino-1-ethyl-3,5-dipentyl-1,2,4-triazolium,
4-methylamino-1-ethyl-3,5-di-(3-methylbutyl)-1,2,4-triazolium,
4-methylamino-1- <i>n</i> -propyl-3,5-di- <i>n</i> -butyl-1,2,4-triazolium,
4-methylamino-1- <i>n</i> -pentyl-3,5-di- <i>n</i> -butyl-1,2,4-triazolium,
4-methylamino-1,3,5-tri- <i>n</i> -butyl-1,2,4-triazolium,
4-ethylamino-1,3,5-tri- <i>n</i> -butyl-1,2,4-triazolium,
4-ethylamino-1-(3-methylbutyl)-3,5-di- <i>n</i> -butyl-1,2,4-triazolium,
4-ethylamino-1-isobutyl-3,5-di- <i>n</i> -butyl-1,2,4-triazolium,
4- <i>n</i> -pentylamino-1-(3-methylbutyl)-3,5-diethyl-1,2,4-triazolium,
4-methylamino-1-allyl-3,5-di-(3-methylbutyl)-1,2,4-triazolium,
4- <i>n</i> -propylamino-1- <i>n</i> -hexyl-3,5-diethyl-1,2,4-triazolium,
4- <i>n</i> -pentylamino-1- <i>n</i> -butyl-3,5-diethyl-1,2,4-triazolium,
especially the chlorides, bromides, methyl sulphates and ethyl sulphates thereof. | 15 |
| 20 | The present compounds are pesticides and plant growth regulants. The
compounds are particularly active on plant physiology, affecting the growth of
plants so that the compounds may be used as herbicides or plant growth regulants.
They are also fungicides. They are outstandingly useful for controlling
monocotyledonous or dicotyledonous weeds in crops. Thus, they are particularly
active in combating wild oats, <i>Avena fatua</i> , <i>A. sterilis</i> and <i>A. ludoviciana</i> , in wheat and
barley, killing or retarding the wild oats so that the wheat or barley can grow on and
smother them. They may also be used to combat weeds in other crops which may
be subject to infestation by wild oats, such as sugarbeet, soy beans, forage legumes,
maize, french and navy beans, ryegrass, brassicas (particularly oil seed rape), flax, | 20 |
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sunflower, peas or potatoes. They may also be used to combat weeds in crops such as cotton, sorghum, peanuts, rice, sugar cane, tobacco or tomatoes. Besides combating wild oats, they also combat blackgrass (*Alopecurus myosuroides*), bentgrass (*Agrostis spp.*), barnyardgrass (*Echinochloa crusgalli*) and crabgrass (*Digitaria spp.*). Activity has also been shown against pigweed (*Amaranthus retroflexus*) and yellow nutsedge. For use as fungicides, the compounds are preferably employed to combat fungal diseases of plants, e.g. plantation crops such as tobacco and food crops such as cereals, potatoes, French or navy beans, tomatoes or rice, especially wheat or barley.

The present compounds are normally employed in the form of compositions, which can be prepared by admixing the ingredients. Usually the compositions are initially produced in the form of concentrates, e.g. containing 0.5—85% of the present compound, and these are diluted with water or hydrocarbon, usually water, for application, generally such that the concentration of the compound is 0.05—5%, though in ultra low volume application the concentration may be higher, e.g. up to 20%. Percentages and parts in this specification are by weight unless otherwise indicated.

The compositions normally contain a surface active agent and/or a carrier.

The carrier may be a liquid, e.g. water (e.g. water used to dilute a concentrate for application). If water is employed as carrier in a concentrate, an organic solvent may also be present as carrier, though this is not usually employed. A surface active agent may advantageously be present.

Those compounds soluble in water may be used as aqueous solutions with or without a surface active agent.

The carrier may be a liquid other than water, for example an organic solvent, such as a water immiscible solvent, e.g. a hydrocarbon which boils within the range 130—270°C, in which the compound is dissolved or suspended. A concentrate containing a water immiscible solvent suitably also contains a surface active agent so that the concentrate acts as a self-emulsifiable oil on admixture with water. The liquid may be a water-miscible solvent e.g. 2-methoxy ethanol, methanol, propylene glycol, diethylene glycol, diethylene glycol monoethyl ether, formamide or methylformamide.

The carrier may be a solid, which may be finely divided. Examples of suitable solids are limestone, clays, sand, mica, chalk, attapulgite, diatomite, perlite, sepiolite, silicas, silicates, lignosulphonates, peat and solid fertilizers. The carrier can be of natural or synthetic origin or can be a modified natural material.

Wettable powders soluble or dispersible in water may be formed by admixing the compound in particulate form with a particulate carrier or spraying molten compound on to the particulate carrier, admixing a wetting agent and a dispersing agent and finely grinding the whole powder mixture.

An aerosol composition may be formed by admixing the compound with a propellant e.g. a polyhalogenated alkane such as dichlorodifluoromethane, and suitably also with a solvent.

A flowable suspension concentrate may be formed if the compound has a low water solubility by grinding the compound with water, a wetting agent and a suspending agent.

A flowable suspension concentrate wherein the carrier is a hydrocarbon which boils within the range 130—270°C rather than water may be formed.

Thus the present composition can for example be solid (e.g. dust or granules) and contain a solid carrier or liquid (e.g. an emulsifiable concentrate) and contain a liquid carrier which is a hydrocarbon which boils within the range 130—270°C.

The term 'surface active agent' is used in the broad sense to include materials variously called emulsifying agents, dispersing agents and wetting agents. Such agents are well known in the art.

The surface active agents used may comprise anionic surface active agents, for example soaps, mono- or di-esters of phosphoric acid with fatty alcohol ethoxylates or salts of such esters, fatty alcohol sulphates such as sodium dodecyl sulphate, sodium octadecyl sulphate or sodium cetyl sulphate, ethoxylated fatty alcohol sulphates, ethoxylated alkylphenol sulphates, lignin sulphonates, petroleum sulphonates, alkyl-aryl sulphonates such as alkyl-benzene sulphonates or lower alkyl-naphthalene sulphonates e.g. butyl-naphthalene sulphonate, salts of sulphonated naphthaleneformaldehyde condensates, salts of sulphonated phenol-formaldehyde condensates, or more complex sulphonates such as the amide sulphonates e.g. the sulphonated condensation product of oleic acid and N-methyl

taurine or the dialkyl sulphosuccinates e.g. the sodium sulphonate of dioctyl succinate. Anionic surface active agents may tend to result in precipitation if employed in some formulations with the present, cationic, compounds. Any surface active agent should be so chosen of course as to avoid this for any particular formulation envisaged.

The surface active agents may also comprise non-ionic agents, for example condensation products of fatty acid esters, fatty alcohols, fatty acid amides or fatty-, alkyl- or alkenyl-substituted phenols with ethylene oxide, fatty esters of polyhydric alcohol ethers e.g. sorbitan fatty acid esters, condensation products of such esters with ethylene oxide e.g. polyoxyethylene sorbitan fatty acid esters, block copolymers of ethylene oxide and propylene oxide, acetylenic glycols such as 2,4,7,9-tetramethyl-5-decyn-4,7-diol, or ethoxylated acetylenic glycols.

The surface active agents may also comprise cationic agents, for example alkyl- and/or aryl-substituted quaternary ammonium compounds such as cetyl trimethylammonium bromide or ethoxylated tertiary fatty amines.

Preferred surface active agents include ethoxylated fatty alcohol sulphates, lignin sulphonates, alkyl-aryl sulphonates, salts of sulphonated naphthalene-formaldehyde condensates, salts of sulphonated phenol-formaldehyde condensates, dialkyl sulphosuccinates, alkyl phenol ethoxylates, and fatty alkyl ethoxylates.

Non-ionic surface active agents are preferred.

Higher quantities of surface active agent, e.g. 5—50% of concentrate, than is normally present in commercial pesticidal or plant growth regulant compositions have been found to increase considerably the activity of the present compounds, even in some cases to several times the original activity.

The surface active agent employed to produce this potentiating effect may be selected from those described above. It is preferably a non-ionic surface active agent, especially an alkyl-substituted phenol condensed with ethylene oxide, e.g. tributylphenol condensed with 11 moles of ethylene oxide (available under the trade mark Sapogenat T110). The potentiating surface active agent may be admixed with the present compound for instance at the point of use, e.g. in a spray tank, or before, e.g. in a concentrate. Preferably the amount of potentiating surface active agent applied in a spray of the present compound is 0.1—5%, especially 1%.

The present active compound may be admixed with another pesticide, e.g. herbicide, insecticide or fungicide, or with another plant growth regulant. The invention provides a one pack presentation, in which the present compound is already mixed with other pesticide or plant growth regulant, and also a single package designed to hold the present compound and other pesticide or plant growth regulant in separate containers, for mixing, e.g. in a spray tank, for application. Particular advantages are obtained with mixtures with another herbicide. The present compound may be used sequentially with another herbicide, e.g. one herbicide applied before planting or before emergence of a crop and the other herbicide applied after emergence of the crop.

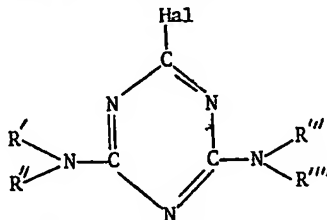
The other herbicide may be for example one or more of a phenoxyaliphatic acid, substituted urea, triazine, phenol, nitrile, bipyridylum compound, substituted benzoic acid, halogenated aliphatic acid, carbamate, thiocarbamate, chloroacetamide, diazine or arsenic herbicide. In respect of selective herbicidal compositions for post-emergence use, the present compound may be used in admixture with for example a substituted phenoxyaliphatic acid; in respect of selective herbicidal compositions for pre-emergence use, the present compound may be used in admixture with for example a substituted urea or triazine; in respect of sequential selective herbicidal use, one may apply for example before emergence of the crop S-2,3-dichloroallyl di-isopropylthiocarbamate or S-2,3,3-trichloroallyl di-isopropylthiocarbamate and the present compound after emergence of the crop.

The phenoxyaliphatic acid generally comprises alkyl and/or halogen substituted phenoxyaliphatic acids, and their salts, for example alkali metal, amine and alkanolamine salts, and functional derivatives, for example esters and amides. These compounds may be of activity such that they are recognised as commercial herbicides, or may be of only slight herbicidal activity. Examples of the substituted phenoxyaliphatic acids which may be mentioned include 2,4-dichlorophenoxyacetic acid, 2-(2,3-dichlorophenoxy)propionic acid, 2-methyl-4-chlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid, gamma-2,4-dichlorophenoxybutyric acid, gamma-2-methyl-4-chloro-phenoxybutyric acid, alpha-2-methyl-4-

chlorophenoxypropionic acid, 2-(4-[2,4-dichlorophenoxy]phenoxy)propionic acid and 2-(4-[4-chlorophenoxy]phenoxy)propionic acid.

The substituted urea generally comprises a tri- or tetra-substituted urea such as N'-(3-chloro-4-methoxyphenyl)-N,N-dimethylurea, N'-(3-chloro-4-methylphenyl)-N,N-dimethylurea, N'-parachlorophenyl-N,N-dimethylurea, N-butyl-N'-(3,4-dichlorophenyl)-N-methylurea, N'-parachlorophenyl-O,N,N-trimethylisourea, N'-p-chlorophenyl-N-methoxy-N-methylurea, N,N-dimethyl-N'-phenylurea, 3-(4-bromophenyl)-1-methoxy-1-methylurea, 1-(2-benzothiazolyl)-3-methylurea, N,N-dimethyl-N'-(4-[1-methylethyl]phenyl)urea, N'-(3,4-dichlorophenyl)-N-methoxy-N-methylurea or N,N-dimethyl-N'-[3-(trifluoromethyl)phenyl]urea.

The triazine herbicide generally comprises 2-chloro-4-(1-cyano-1-methylamino)-6-ethylamino-1,3,5-triazine or 2-isopropylamino-4-(3-methoxypropylamino)-6-methylthio-1,3,5-triazine or a compound of the formula:—



where Hal is a halogen atom, OY group or SY group, where Y is an alkyl group, R' and R''' are the same or different and are hydrogen or alkyl and R'' and R'''' are the same or different alkyl groups, such as 2-chloro-4,6-bisethylamino-1,3,5-triazine, 2-chloro-4-ethylamino-6-diethylamino-1,3,5-triazine, 2-chloro-6-ethylamino-4-isopropylamino-1,3,5-triazine or 2,4-bis(isopropylamino)-6-methylthio-1,3,5-triazine.

The phenol herbicide generally comprises 4,6-dinitro-o-cresol, 4,6-dinitro-2-sec-butylphenol or pentachlorophenol. The nitrile herbicide generally comprises 3,5-diiodo-4-hydroxybenzonitrile, 3,5-dibromo-4-hydroxybenzonitrile or 2,6-dichlorobenzonitrile. The bipyridylum herbicide generally comprises 1,1'-dimethyl-4,4'-bipyridylum dichloride or 1,1'-ethylene-2,2'-bipyridylum dibromide. The substituted benzoic acid herbicide generally comprises 2,3,6-trichlorobenzoic acid, 2-methoxy-3,6-dichlorobenzoic acid or N-(1,1-dimethylpropynyl)-3,5-dichlorobenzamide. The halogenated aliphatic acid herbicide generally comprises trichloroacetic acid or 2,2-dichloropropionic acid. The carbamate herbicide generally comprises isopropyl N-(3-chlorophenyl)carbamate, 4-chloro-2-butynyl N-(3-chlorophenyl)carbamate, methyl 3-(m-tolyl-carbamoyloxy)phenylcarbamate or D-N-ethyl-2-(phenylcarbamoyloxy)-propionamide. The thiocarbamate herbicide generally comprises S-ethyl N,N-diisopropylthiocarbamate, S-ethyl N,N-diisobutylthiocarbamate, S-(2,3-dichloroallyl) N,N-diisopropylthiocarbamate, S-ethyl N-ethyl-N-cyclohexylthiocarbamate, S-propylbutylethylthiocarbamate or S-(2,3,3-trichloroallyl) N,N-diisopropylthiocarbamate. The chloroacetamide herbicide generally comprises N,N-diallyl-2-chloroacetamide or N-isopropyl-2-chloroacetanilide. The diazine herbicide generally comprises 5-bromo-6-methyl-3-sec-butyluracil, 3-cyclohexyl-5,6-trimethyleneuracil, 5-amino-4-chloro-2-phenyl-3-pyridazinone or 1,2-dihydro-pyridazine-3,6-dione. The arsenic herbicide generally comprises a salt of methane arsonic acid or cacodylic acid. Other herbicides which may be used as the second herbicide include 1,2-dimethyl-2,5-diphenylpyrazolium ion, ethyl N-benzoyl-N-(3,4-dichlorophenyl)alanine, N-isobutyl-2-oxo-1-imidazolidine-carboxamide, aminotriazole, 2,3-dichloro-1,4-naphthoquinone, 4-amino-3,5,6-trichloropicolinic acid, N,N-dimethyl-2,2-diphenylacetamide, 2,6-dinitro-N,N-dipropyl-4-trifluoromethylaniline, N-butyl-N-ethyl-2,6-dinitro-4-trifluoromethylaniline, S,S,S-tributyl phosphorotrithioate, 2-ethoxy-2,3-dihydro-3,3-dimethyl-5-benzofuranyl methylsulphonate, 4-chloro-2-oxobenzothiazolin-3-yl acetic acid, 3-isopropyl-2,1,3-benzothiadiazinon-(4)-2,2-dioxide, 3,5-dibromo-4-hydroxybenzaldehyde 2,4-dinitrophenyloxime, methyl 2-chloro-3-(4-chlorophenyl)propionate, 2-chloroethyltrimethylammonium chloride, 4-methylsulphonyloxy-2-butynyl m-chlorocarbanilate, isopropyl 2-(N-benzoyl-3-chloro-4-fluoroanilino)propionate, methyl 2-(N-benzoyl-3-chloro-4-fluoroanilino)propionate, 2-chloro-N-(1,3-dioxolan-2-ylmethyl)-2',6'-dimethylacetanilide, 2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-trifluoromethylbenzene, methyl 2-(4-[2',4'-dichlorophenoxy]phenoxy)propionate or isobutyl 2-(4-[4'-chlorophenoxy]phenoxy)propionate.

The other herbicide may particularly be another herbicide which combats wild oats in cereal crops.

In particular embodiments, the present compound and particularly one specified above, advantageously one specified as being preferred or especially preferred, e.g.

4-methylamino-1-ethyl-3,5-diphenyl-1,2,4-triazolium chloride or ethyl sulphate or especially 4-methylamino-1-methyl-3,5-dipentyl-1,2,4-triazolium chloride or methyl sulphate is used (a) in admixture with 4-chloro-2-butynyl 3-chlorophenyl-carbamate, 1,2-dimethyl-3,5-diphenylpyrazolium ion, alpha-2-methyl-4-chlorophenoxypropionic acid, N'-(3-chloro-4-methoxyphenyl)-N,N-dimethylurea, N'-(3-chloro-4-methylphenyl)-N,N-dimethylurea or ethyl N-benzoyl-N-(3,4-dichlorophenyl)aniline, or (b) after emergence of the crop following use before emergence of the crop of S-2,3-dichloroallyl di-isopropylthiocarbamate or S-2,3,3-trichloroallyl di-isopropylthiocarbamate.

The present compound may be used in admixture or sequence with another fungicide, particularly another cereal fungicide. The other fungicide may be for instance one or more of maneb (polymeric manganese ethylenebisdithiocarbamate), zineb (zinc ethylenebisdithiocarbamate), mancozeb (which can be regarded as a mixture of maneb and zineb), thiram (tetramethylthiuram disulphide), ditalimfos (O,O-diethyl phthalimidophosphonothioate), tridemorph (2,6-dimethyl-4-tridecylmorpholine), fluotrimazole (1-[diphenyl-(3-trifluoromethylphenyl)methyl]-1,2,4-triazole), ethirimol (5-butyl-2-ethylamino-4-hydroxy-6-methylpyrimidine), trifluorine (1,4-di[2,2,2-trichloro-1-formamido-ethyl]piperazine), pyracarbolid (3,4-dihydro-6-methylpyran-5-carboxanilide), zineb-ethylene thiuramdisulphide adduct, carbendazim (methyl benzimidazol-2-ylcarbamate), captafol (3a,4,7,7a-tetrahydro-N-[1,1,2,2-tetrachloroethane-sulphenyl]phthalimide), thiophanate (1,2-di[3-ethoxycarbonyl-2-thioureido]-benzene), proprineb (polymeric zinc propylenebisdithiocarbamate), oxycarboxin (2,3-dihydro-6-methyl-5-phenylcarbamoyl-1,4-oxathiin 4,4-dioxide), quintozene (pentachloronitrobenzene), benomyl (methyl 1-[butylcarbamoyl]benzimidazol-2-ylcarbamate) and benadil (2-iodobenzanilide).

The present compound may be used in admixture or sequence with an insecticide, particularly a cereal insecticide. The insecticide may be for instance one or more of demeton-S-methyl (S-2-ethylthioethyl O,O-dimethyl phosphorothioate), dimethoate (O,O-dimethyl S-methylcarbamoylmethyl phosphorodithioate), formothion (S-[N-formyl-N-methylcarbamoylmethyl] O,O-dimethyl phosphorodithioate), oxydemeton-methyl (S-2-ethylsulphinylethyl O,O-dimethyl phosphorothioate), pirimicarb (2-dimethylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate), thiometon (S-2-ethylthioethyl O,O-dimethyl phosphorodithioate), BHC (benzene hexachloride), aldrin (1,2,3,4,10,10-hexachloro-1,4a,4,5,8,8a-hexahydro-exo-1,4-endo-5,8-dimethanonaphthalene), fenitrothion (O,O-dimethyl O-4-nitro-*m*-tolyl phosphorothioate), omethoate (O,O-dimethyl S-methylcarbamoylmethyl phosphorothioate), pirimiphos-methyl (O-2-diethylamino-6-methylpyrimidin-4-yl O,O-dimethyl phosphorothioate) and DDT (1,1,1-trichloro-2,2-di[chlorophenyl]ethane).

The ratio of the present compound to the other pesticide or plant growth regulant may vary over a wide range according to the particular compounds involved and the intended use. In general the ratio of present compound to other pesticide or plant growth regulant lies in the range 1:0.1 to 1:15.

The present compounds may be in admixture with non-phytotoxic oils, e.g. Agri-Oil Plus, Sun Oil 11E or Fyzol E.

The compounds may be in admixture with an antidote (a substance having the property of improving the selectivity of herbicides), e.g. N,N-diallyl-2,2-dichloroacetamide or 1,8-naphthalic anhydride.

The compounds may be in admixture with ammonium sulphate which improves the activity of some herbicides. For this, it may be applied for example at 0.5—20, e.g. 2, kg per hectare, and may be admixed with the present compound in a spray tank immediately before use.

The compounds may be in admixture with fertilizers.

When a compound of formula II is employed in which X^o represents an equivalent of an anion of a strong acid, e.g. when the compound is an alkyl sulphate, the compound may be in admixture with a base, e.g. sodium acetate or

sodium hydroxide, so that the compositions applied in use are not so acid as to harm the application equipment or a crop treated.

In the use of the present compounds as total herbicides, high rates of application, for example at least 10 kg per hectare, such as 10—25 kg per hectare, of the compounds are usually required, unless they are mixed with other herbicides, in which case the rate can be reduced.

In the use of the present compounds as selective herbicides, the rate of application is usually much lower and may be for example 0.5—10, e.g. 0.5—8, kg per hectare, such as 1—4 kg per hectare.

In the use of the compounds as plant growth regulants, low rates of application are usually required such as 0.1—4, e.g. 0.5—1, kg per hectare.

For use as fungicides, the compounds are generally applied at a rate of 1—6 kg per hectare.

Since it is the cation in the compounds of formula III which is responsible for the activity, it is the amount of such cation rather than of the compound as a whole which is to be counted in the rates specified above.

The present compounds may be applied to plants, the soil, land, aquatic areas or inanimate or stored materials, e.g. textiles, paper, leather or wood, susceptible to fungal attack. They are preferably used as herbicides, particularly selective herbicides, especially for selectively combating weeds by application to a locus at which a crop e.g. a food crop and especially a cereal crop such as wheat or barley is growing or is to grow. Thus, the compounds may be applied pre- or post-planting of the crop. They may be employed for pre-emergence use or preferably post-emergence use. They may be used especially to combat wild oats particularly in cereal crops. The compounds may be used as fungicides, particularly for combating fungal diseases of plants, e.g. cereal powdery mildew. Thus, the compounds may be used to protect plants from weeds and fungus.

The invention is illustrated by the following Examples.

Example 1.

A mixture of 4-amino-3,5-diphenyl-1,2,4-triazole (236 parts) and dimethyl sulphate (126 parts) was heated at 200°C for 10 minutes. The product was then cooled and ground up under petroleum and then filtered off. The white solid was then dried to give 4-amino-1-methyl-3,5-diphenyl-1,2,4-triazolium sulphate (341 parts, 94% yield), melting point 52—60°C.

Found: C, 52.55; H, 5.34; N, 15.04%

$C_{18}H_{18}N_4O_4S$ requires: C, 53.02; H, 5.01; N, 15.46%

Example 2.

A mixture of 4-amino-3,5-diphenyl-1,2,4-triazole (236 parts) and dimethyl sulphate (126 parts) was heated at 200°C for 10 minutes. The resulting hot oil was dissolved in water (2,000 parts), cooled to room temperature and treated with normal aqueous sodium hydroxide solution (1,000 parts). The mixture was then heated at 100°C for two hours with occasional stirring. The solid product was filtered off, washed with water and recrystallised from isopropanol to give 4-methylamino-3,5-diphenyl-1,2,4-triazole (134 parts, 54% yield) (melting point 195—196°C). This product was then heated at 200°C for 10 minutes with dimethyl sulphate (67 parts). The resulting oil was cooled to solidify and ground up under petroleum. The white solid was filtered off and dried to give 1-methyl-4-methylamino-3,5-diphenyl-1,2,4-triazolium methyl sulphate (169 parts, 84% yield).

Found: C, 53.95; H, 5.34; N, 14.57%

$C_{17}H_{20}N_4O_4S$ requires: C, 54.24; H, 5.36; N, 14.88%

Examples 3 to 65.

The following compounds were prepared by methods analogous to those described in Examples 1 and 2, employing the appropriate starting material and an appropriate sulphate or halide quaternising agent:

3. 4-amino-1-methyl-3,5-diphenyl-1,2,4-triazolium *p*-toluenesulphonate, mp 57—60°.

4. 4-amino-1-methyl-3,5-bis(4-methylphenyl)-1,2,4-triazoliummethyl sulphate, mp 62—66°.

	5. 4-amino-1-methyl-3,5-bis(4-methoxyphenyl)-1,2,4-triazoliummethyl sulphate, mp 54—58°.	
	6. 4-amino-1-ethyl-3,5-bis(4-methoxyphenyl)-1,2,4-triazolium ethyl sulphate, hygroscopic solid.	
5	7. 4-amino-1-ethyl-3,5-bis(4-chlorophenyl)-1,2,4-triazolium ethyl sulphate, mp 62—65°.	5
	8. 4-amino-1-ethyl-3,5-bis(4-methylphenyl)-1,2,4-triazolium ethyl sulphate, mp 36—42°.	
10	9. 4-amino-1-ethyl-3,5-bis(4-methoxyphenyl)-1,2,4-triazolium ethyl sulphate, mp 36—42°.	10
	10. 4-methylamino-1-methyl-3,5-bis(4-methoxyphenyl)-1,2,4-triazolium methyl sulphate, mp 56—58°.	
	11. 4-ethylamino-1-methyl-3,5-diphenyl-1,2,4-triazolium methyl sulphate, mp 87—90°.	
15	12. 4-methylamino-1-ethyl-3,5-diphenyl-1,2,4-triazolium ethyl sulphate, m.p. 148—51°.	15
	13. 4-methylamino-1-ethyl-3,5-bis(4-methylphenyl)-1,2,4-triazolium ethyl sulphate, hygroscopic solid.	
	14. 4-amino-1-benzyl-3,5-diphenyl-1,2,4-triazolium chloride, mp 96—98°.	
20	15. 4-amino-3,5-dicyclohexyl-1-methyl-1,2,4-triazolium methyl sulphate, m.p. 160—168°C.	20
	16. 4-methylamino-3,5-dicyclohexyl-1-methyl-1,2,4-triazolium methyl sulphate, m.p. 116—120°C.	
25	17. 4-amino-1-methyl-3,5-dipentyl-1,2,4-triazolium methyl sulphate, oil.	25
	18. 4-methylamino-1-methyl-3,5-dipentyl-1,2,4-triazolium methyl sulphate, oil.	
	19. 4-ethylamino-1-methyl-3,5-dipentyl-1,2,4-triazolium methyl sulphate, oil.	
	20. 4-methylamino-1-ethyl-3,5-dipentyl-1,2,4-triazolium ethyl sulphate, oil.	
	21. 4-amino-1-methyl-3,5-di(3-methylbutyl)-1,2,4-triazolium methyl sulphate, oil.	
30	22. 4-methylamino-1-ethyl-3,5-dibutyl-1,2,4-triazolium ethyl sulphate oil.	30
	23. 4-ethylamino-1-methyl-3,5-dibutyl-1,2,4-triazolium methyl sulphate, oil.	
	24. 3,5-dibutyl-1-ethyl-4-ethylamino-1,2,4-triazolium ethyl sulphate, oil.	
	25. 4-amino-1-ethyl-3,5-di(3-methylbutyl)-1,2,4-triazolium ethyl sulphate, m.p. 62—66°C.	
35	26. 4-amino-1-methyl-3,5-dicyclopentyl-1,2,4-triazolium methyl sulphate, m.p. 141—144°C.	35
	27. 1-methyl-4-methylamino-3,5-di(3-cyclohexen-1-yl)-1,2,4-triazolium methyl sulphate, m.p. 60°C.	
	28. 4-amino-1-methyl-3,5-diheptyl-1,2,4-triazolium methyl sulphate, oil.	
40	29. 4-amino-1-methyl-3,5-di(3,4-xylyl)-1,2,4-triazolium methyl sulphate, m.p. 52—55°C.	40
	30. 4-amino-1-ethyl-3,5-diheptyl-1,2,4-triazolium ethyl sulphate, oil.	
	31. 4-methylamino-1-ethyl-3,5-di(3-methylbutyl)-1,2,4-triazolium ethylsulphate, oil.	
	32. 4-methylamino-1- <i>n</i> -propyl-3,5-di- <i>n</i> -butyl-1,2,4-triazolium bromide, oil.	
	33. 4-methylamino-1- <i>n</i> -pentyl-3,5-di- <i>n</i> -butyl-1,2,4-triazolium bromide, oil.	
45	34. 4-methylamino-1,3,5-tri- <i>n</i> -butyl-1,2,4-triazolium bromide, m.p. 65—67°C.	45
	35. 4-ethylamino-1,3,5-tri- <i>n</i> -butyl-1,2,4-triazolium bromide, m.p. 37—40°C.	
	36. 4-ethylamino-1-(3-methylbutyl)-3,5-di- <i>n</i> -butyl-1,2,4-triazolium bromide, m.p. 54—56°C.	
50	37. 4-ethylamino-1-isobutyl-3,5-di- <i>n</i> -butyl-1,2,4-triazolium bromide, oil.	50
	38. 4- <i>n</i> -pentylamino-1-(3-methylbutyl)-3,5-diethyl-1,2,4-triazolium bromide, hygroscopic solid.	
	39. 4-methylamino-1-allyl-3,5-di(3-methylbutyl)-1,2,4-triazolium bromide, m.p. 97—99°C.	
55	40. 4- <i>n</i> -propylamino-1- <i>n</i> -hexyl-3,5-diethyl-1,2,4-triazolium bromide, hygroscopic solid.	55
	41. 4- <i>n</i> -pentylamino-1- <i>n</i> -butyl-3,5-diethyl-1,2,4-triazolium bromide, hygroscopic solid.	
	42. 4-amino-1- <i>n</i> -hexyl-1,2,4-triazolium bromide, hygroscopic solid.	
60	43. 4-amino-1- <i>n</i> -decyl-3,5-dimethyl-1,2,4-triazolium bromide, hygroscopic solid.	60
	44. 4- <i>n</i> -pentylamino-1- <i>n</i> -pentyl-3,5-dimethyl-1,2,4-triazolium bromide, hygroscopic solid.	
	45. 4- <i>n</i> -pentylamino-1-(3-methylbutyl)-3,5-dimethyl-1,2,4-triazolium bromide, hygroscopic solid.	
65	46. 4- <i>n</i> -hexylamino-1- <i>n</i> -pentyl-3,5-dimethyl-1,2,4-triazolium bromide, m.p. 149—151°C.	65

	47. 4-amino-1- <i>n</i> -nonyl-3,5-diethyl-1,2,4-triazolium bromide, hygroscopic solid.	
	48. 4-amino-1- <i>n</i> -decyl-3,5-diethyl-1,2,4-triazolium bromide, hygroscopic solid.	
	49. 4-methylamino-1-methyl-3,5-di- <i>n</i> -butyl-1,2,4-triazolium methylsulphate, oil.	
5	50. 4-ethylamino-1- <i>n</i> -pentyl-3,5-di- <i>n</i> -butyl-1,2,4-triazolium bromide, m.p. 63—65°C.	5
	51. 4-amino-1-(3-methylbutyl)-3,5-di- <i>n</i> -pentyl-1,2,4-triazolium bromide, m.p. 105—106°C.	
	52. 4-methylamino-1-methyl-3,5-di- <i>n</i> -pentyl-1,2,4-triazolium methylsulphate, oil.	
10	53. 4-ethylamino-1-methyl-3,5-di- <i>n</i> -pentyl-1,2,4-triazolium methylsulphate, oil.	10
	54. 4-amino-1-methyl-3,5-di(3-methylbutyl)-1,2,4-triazolium methylsulphate, oil.	
	55. 4-amino-1-ethyl-3,5-di(3-methylbutyl)-1,2,4-triazolium ethylsulphate, m.p. 62—66°C.	
	56. 4-methylamino-1-methyl-3,5-di-cyclopentyl-1,2,4-triazolium methylsulphate, m.p. 68—70°C.	
15	57. 4-amino-1-methyl-3,5-di- <i>n</i> -octyl-1,2,4-triazolium methylsulphate, oil.	15
	58. 4-methylamino-1-ethyl-3,5-di-cyclopentyl-1,2,4-triazolium ethylsulphate, m.p. 60—66°C.	
	59. 4-amino-1-methyl-3,5-di- <i>n</i> -hexyl-1,2,4-triazolium methyl sulphate, oil.	
20	60. 4-amino-1-ethyl-3,5-di- <i>n</i> -hexyl-1,2,4-triazolium ethylsulphate, oil.	20
	61. 4-amino-1-ethyl-3,5-di- <i>n</i> -octyl-1,2,4-triazolium ethylsulphate, oil.	
	62. 4-methylamino-1-methyl-3,5-di- <i>n</i> -octyl-1,2,4-triazolium methyl sulphate oil.	
	63. 4-methylamino-1-ethyl-3,5-di- <i>n</i> -octyl-1,2,4-triazolium ethylsulphate, oil.	
	64. 4-methylamino-1-methyl-3,5-dicyclohexyl-1,2,4-triazolium methylsulphate, m.p. 116—120°C, and	
25	65. 4-amino-1-methyl-3,5-di-(<i>p</i> -tolyl)-1,2,4-triazolium methylsulphate, m.p. 62—66°C.	25

Example 66.

30	n-Caproic hydrazide (260 parts) and sodium methoxide (108 parts) were dissolved in methanol (100 parts). Ethyl thiobenzoate (332 parts) in methanol (500 parts) was then added to the solution, and the reaction mixture was allowed to stand overnight at room temperature. It was then evaporated to dryness keeping the temperature below 40°C. The residue was then dissolved in ice water (6000 parts), the solution then being acidified to pH=6 with acetic acid and filtered. The solid, after washing with water, was dissolved in water (2500 parts) containing hydrazine hydrate (200 parts) and hydrazine dihydrochloride (42 parts). The solution was heated at reflux for 3 hours under nitrogen and the solid material filtered off and recrystallised from butanol, to yield 202 parts of 4-amino-3- <i>n</i> -pentyl-5-phenyl-1,2,4-triazole, m.p. 190—193°C.	30
35		35

	Analysis:	C	H	N	
40	Calculated:	67.79	7.88	24.33%	40
	Found:	68.01	8.22	24.38%	

45	On reaction with dimethylsulphate and then with diethylsulphate as described in Example 2, a mixture of 4-methylamino-1-ethyl-3-phenyl-5- <i>n</i> -pentyl-1,2,4-triazolium ethylsulphate and 4-methylamino-1-ethyl-3- <i>n</i> -pentyl-5-phenyl-1,2,4-triazolium ethyl sulphate was obtained as an oil.	45
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Examples 67 to 84.

50	Seeds of wheat (<i>Triticum aestivum</i>), barley (<i>Hordeum vulgare</i>) and wild oats (<i>Avena</i> spp) were sown in anodised aluminium pots, 20 cm long × 10 cm wide × 5 cm deep, containing John Innes I potting compost. They were then watered and placed in a controlled environment room (temperature 22°C, relative humidity 65—85%, artificial illumination of 17,000 lux for 14 hours per day) for 14 days. The emergent seedlings were then sprayed with the compounds listed below in aqueous solution containing 2,000 ppm of the condensation product of nonylphenol with ethylene oxide as wetting agent. The dosage rate was equivalent to 2.8 kg of the cation of the compound in 375 litres per hectare. The plants were then returned to the controlled environment room for a further 14 days and visually assessed for herbicidal effect by comparison with untreated controls. Differences from the controls were scored on a scale from 0 to 100 in which 0 signifies no effect and 100 signifies complete suppression and are tabulated below.	50
55		55

Compound	Herbicidal effect		
	Wheat	Barley	Wild oats
4-amino-1-methyl-3,5-diphenyl-1,2,4-triazolium methyl sulphate	0	3	65
4-methylamino-1-methyl-3,5-diphenyl-1,2,4-triazolium methyl sulphate	5	3	75
4-ethylamino-1-methyl-3,5-diphenyl-1,2,4-triazolium methyl sulphate	7	3	55
4-methylamino-1-ethyl-3,5-diphenyl-1,2,4-triazolium ethyl sulphate	4	5	65
4-methylamino-1-ethyl-3,5-bis-(4-methylphenyl)-1,2,4-triazolium ethyl sulphate	8	10	35
4-amino-3,5-dicyclohexyl-1-methyl-1,2,4-triazolium methyl sulphate	0	5	80
4-methylamino-3,5-dicyclohexyl-1-methyl-1,2,4-triazolium methyl sulphate	5	5	70
4-amino-1-methyl-3,5-dipentyl-1,2,4-triazolium methyl sulphate	5	5	70
4-methylamino-1-methyl-3,5-dipentyl-1,2,4-triazolium methyl sulphate	20	5	80
4-ethylamino-1-methyl-3,5-dipentyl-1,2,4-triazolium methyl sulphate	20	20	70
4-methylamino-1-ethyl-3,5-dipentyl-1,2,4-triazolium ethyl sulphate	30	20	70
4-amino-1-methyl-3,5-di(3-methylbutyl)-1,2,4-triazolium methyl sulphate	5	5	80
4-methylamino-1-ethyl-3,5-di butyl-1,2,4-triazolium ethyl sulphate	5	5	80
4-ethylamino-1-methyl-3,5-di butyl-1,2,4-triazolium methyl sulphate	5	5	80
3,5-di butyl-1-ethyl-4-ethylamino-1,2,4-triazolium ethyl sulphate	10	5	90
4-amino-1-ethyl-3,5-di(3-methylbutyl)-1,2,4-triazolium ethyl sulphate	5	5	80
4-amino-1-methyl-3,5-dicyclopentyl-1,2,4-triazolium methyl sulphate	5	5	70
1-methyl-4-methylamino-3,5-di(3-cyclohexen-1-yl)-1,2,4-triazolium methyl sulphate	5	5	70

Examples 85—94.

In a test as described in Examples 67 to 84, and against additional plant species, the following results were obtained.

Compound	Herbicidal effect						
	Wheat	Barley	Wild oats	Black grass	Barn yard grass	Crab grass	Yellow Nuts edge
4-methylamino-1-ethyl- 3,5-di-(3-methylbutyl)- 1,2,4-triazolium ethyl sulphate	40	10	100	80	80	60	NT
4-methylamino-1- <i>n</i> - propyl-3,5-di- <i>n</i> -butyl- 1,2,4-triazolium bromide	40	5	100	70	90	80	75
4-methylamino-1,3,5- tri- <i>n</i> -butyl-1,2,4- triazolium bromide	40	5	100	60	90	80	NT
4-ethylamino-1,3,5- tri- <i>n</i> -butyl-1,2,4- triazolium bromide	40	20	100	80	100	80	NT
4-ethylamino-1-isobutyl- 3,5-di- <i>n</i> -butyl-1,2,4- triazolium bromide	30	10	100	80	90	90	NT
4- <i>n</i> -pentylamino-1-(3- methylbutyl)-3,5- diethyl-1,2,4-triazolium bromide	50	15	100	90	90	90	NT
4-methylamino-1-allyl- 3,5-di-(3-methylbutyl)- 1,2,4-triazolium bromide	40	30	100	70	90	90	NT
4- <i>n</i> -propylamino-1- <i>n</i> - hexyl-3,5-diethyl-1,2,4- triazolium bromide	40	10	100	70	100	90	NT
4- <i>n</i> -pentylamino-1- <i>n</i> - butyl-3,5-diethyl- 1,2,4-triazolium bromide	50	15	100	80	90	70	NT
Mixture of 4-methylamino- 1-ethyl-3-phenyl-5- <i>n</i> - pentyl and 4-methylamino- 1-ethyl-3- <i>n</i> -pentyl-5- phenyl-1,2,4-triazolium ethyl sulphate	20	20	70	30	30	80	NT

NT = not tested.

Examples 95—101.

In a test as described in Examples 67 to 84, but against different plant species, and at an application rate of 0.7 kg/ha, the following results were obtained:

Compound	Herbicidal effect						
	Chick weed	May weed	Cleavers	Pale Persicaria	Fathen	Corn Mari gold	Pig weed
4-methylamino-1- <i>n</i> -pentyl-3,5-di- <i>n</i> -butyl-1,2,4-triazolium bromide	30	30	80	90	70	90	70
4-ethylamino-1,3,5-tri- <i>n</i> -butyl-1,2,4-triazolium bromide	30	30	90	100	80	100	90
4-ethylamino-1-(3-methylbutyl)-3,5-di- <i>n</i> -butyl-1,2,4-triazolium bromide	80	70	100	100	80	100	100
4-ethylamino-1-isobutyl-3,5-di- <i>n</i> -butyl-1,2,4-triazolium bromide	50	50	90	100	90	90	90
4- <i>n</i> -pentylamino-1-(3-methylbutyl)-3,5-diethyl-1,2,4-triazolium bromide	40	40	100	100	90	100	90
4- <i>n</i> -propylamino-1- <i>n</i> -hexyl-3,5-diethyl-1,2,4-triazolium bromide	40	100	90	100	100	100	100
4- <i>n</i> -pentylamino-1- <i>n</i> -butyl-3,5-diethyl-1,2,4-triazolium bromide	80	80	80	100	90	90	80

Examples 102—104.

Aqueous acetone solutions containing 500 mg per litre (based on the cation) of the compounds listed below together with 125 mg per litre of a non-ionic wetting agent were sprayed on the foliage of young barley plants (3 leaf stage).

The treated plants, together with controls treated with wetting agent alone, were inoculated 24 hours after the chemical application with spores of cereal powdery mildew, *Erysiphe graminis*.

The plants were then placed in a controlled environment room held at 16°C and 60% relative humidity for 10 days when the percentage of disease control was assessed.

The degree of control by the compounds was found to be:

Compound	% control
4-amino-3,5-diheptyl-1-methyl-1,2,4-triazolium methyl sulphate	98
1-methyl-4-methylamino-3,5-dipentyl-1,2,4-triazolium methyl sulphate	90
1-methyl-4-methylamino-3,5-dicyclohexyl-1,2,4-triazolium methyl sulphate	92

Example 105.

A wettable powder formulation containing 50% of 1-methyl-4-methylamino-3,5-diphenyl-1,2,4-triazolium cation was prepared by fluid energy milling the following:

5	1-methyl-4-methylamino-3,5-diphenyl-1,2,4-triazolium methyl sulphate	74.3%	5
	'Arkopon T highly concentrated' (64% sodium N-oleoyl-N-methyltauride)	5%	
	China clay	20.7%	10

Example 106.

A wettable powder formulation containing 50% of 1-ethyl-4-methylamino-3,5-diphenyl-1,2,4-triazolium cation was prepared by fluid energy milling the following:

10	1-ethyl-4-methylamino-3,5-diphenyl-1,2,4-triazolium ethyl sulphate	72.4%	
15	'Arkophon T highly concentrated' (64% sodium N-oleoyl-N-methyltauride)	5%	15
	China clay	22.6%	

Example 107.

A wettable powder formulation containing 50% of 4-ethylamino-1-methyl-3,5-diphenyl-1,2,4-triazolium cation was prepared by fluid energy milling the following:

20	4-ethylamino-1-methyl-3,5-diphenyl-1,2,4-triazolium methyl sulphate	69.9%	20
	'Arkophon T highly concentrated' (64% sodium N-oleoyl-N-methyltauride)	5%	
25	China clay	25.1%	25

Example 108.

A wettable powder formulation containing 50% of 1-methyl-4-methylamino-3,5-di(*m*-tolyl)-1,2,4-triazolium cation was prepared by fluid energy milling the following:

30	1-methyl-4-methylamino-3,5-di(<i>m</i> -tolyl)-1,2,4-triazolium methyl sulphate	69%	30
	'Arkophon T highly concentrated' (64% sodium N-oleoyl-N-methyltauride)	5%	
	China clay	26%	

Example 109.

A 40% aqueous concentrate of 4-amino-1-methyl-3,5-diphenyl-1,2,4-triazolium cation was prepared by admixing the following:

	4-amino-1-methyl-3,5-diphenyl-1,2,4-triazolium methyl sulphate	57.8% weight/volume	
40	water	to 100%	

Example 110.

An 8% aqueous concentrate of 1-ethyl-4-ethylamino-3,5-diphenyl-1,2,4-triazolium cation was prepared by admixing the following:

	1-ethyl-4-ethylamino-3,5-diphenyl-1,2,4-triazolium ethyl sulphate	11.4% weight/volume	
45	water	to 100%	45

Example 111.

A 5% aqueous concentrate of 1-ethyl-4-methylamino-3,5-di(*m*-tolyl)-1,2,4-triazolium cation was prepared by admixing the following:

5	1-ethyl-4-methylamino-3,5-di(<i>m</i> -tolyl)-1,2,4-triazolium ethyl sulphate	7% weight/volume	5
	water	to 100%	

Example 112.

A buffered 4.8% aqueous concentrate of 1-ethyl-4-methylamino-3,5-di(*m*-tolyl)-1,2,4-triazolium cation was prepared by admixing the following:

10	1-ethyl-4-methylamino-3,5-di(<i>m</i> -tolyl)-1,2,4-triazolium ethyl sulphate	6.7% weight/volume	10
	anhydrous sodium acetate	1.0% weight/volume	
	water	to 100%	

Example 113.

A 10% aqueous alcoholic concentrate of 1-methyl-4-methylamino-3,5-dipentyl-1,2,4-triazolium cation was prepared by admixing the following:

15	1-methyl-4-methylamino-3,5-dipentyl-1,2,4-triazolium methyl sulphate	14.4% weight/volume	15
20	1-molar sodium hydroxide solution to pH 7	approx. 3.6% by volume	20
	2-ethoxyethanol	5% by volume	
	n-butanol	to 100%	

Example 114.

A 10% aqueous alcoholic concentrate of 1-ethyl-4-methylamino-3,5-dipentyl-1,2,4-triazolium cation was prepared by admixing the following:

25	1-ethyl-4-methylamino-3,5-dipentyl-1,2,4-triazolium ethyl sulphate	14.7% weight/volume	25
	1-molar sodium hydroxide solution, to pH 5	approx. 1.25% by volume	
30	n-butanol	to 100%	30

Examples 115—127.

Seeds of peas (*Pisum sativum*), mustard (*Sinapis alba*), linseed (*Linum usitatissimum*), ryegrass (*Lolium sp.*), oats (*Avena sativa*), sugar beet (*Beta vulgaris*) and French beans (*Phaseolus vulgaris*) were sown in anodised aluminium pans, 19 cm long × 9.5 cm wide × 5 cm deep containing John Innes I potting compost. They were then watered and placed in a controlled environment room (temperature 22°C, relative humidity 65—85%, artificial illumination 13,000 lux for 14 hours per day). After 14 days, the seedlings were sprayed with aqueous solutions or suspensions of the compounds listed below at rates equivalent to 11.2 and 2.8 kg of active ingredient cation in 450 litres per hectare.

After 7 days growth in the controlled environment room, the plants were visually assessed for any herbicidal or growth regulant response, all differences from untreated controls being scored on a 0 to 100 scale in which 0 signifies no effect and 100 signifies complete kill. The results are tabulated below:

Compound	Rate Kg/ha	Peas	Mustard	Linseed	Herbicidal Effect			
					Ryegrass	Oats	Sugarbeet	Beans
1-methyl-3,5-dicyclohexyl-4-amino-1,2,4-triazolium methyl sulphate	11.2	30	70	30	60	60	20	30
1-methyl-3,5-dicyclohexyl-4-methylamino-1,2,4-triazolium methyl sulphate	11.2 2.8	40 30	40 20	80 30	60 10	80 60	40 30	60 20
1-methyl-3,5-dipentyl-4-amino-1,2,4-triazolium methyl sulphate	11.2 2.8	60 20	70 40	100 30	30 20	90 80	100 30	90 30
1-methyl-3,5-dipentyl-4-methylamino-1,2,4-triazolium methyl sulphate	11.2 2.8	90 60	100 70	100 70	70 30	100 80	100 40	90 70
1-methyl-3,5-dipentyl-4-ethylamino-1,2,4-triazolium methyl sulphate	11.2 2.8	100 70	100 40	100 100	70 20	90 70	100 30	90 90
1-ethyl-3,5-dipentyl-4-methylamino-1,2,4-triazolium ethyl sulphate	11.2 2.8	90 70	100 80	100 80	100 20	90 60	100 80	100 70
1-methyl-3,5-di(3-methylbutyl)-4-amino-1,2,4-triazolium methyl sulphate	11.2 2.8	70 20	60 20	90 30	70 10	90 70	100 20	60 20
1-ethyl-3,5-diethyl-4-methylamino-1,2,4-triazolium ethyl sulphate	11.2 2.8	80 30	90 20	100 50	70 10	90 70	100 30	40 10
1-methyl-3,5-diethyl-4-ethylamino-1,2,4-triazolium methyl sulphate	11.2 2.8	70 10	80 20	100 20	40 5	90 60	100 10	70 30
1-ethyl-3,5-diethyl-4-ethylamino-1,2,4-triazolium ethyl sulphate	11.2 2.8	70 30	90 80	100 90	90 30	100 90	100 90	90 70
1-ethyl-3,5-di(3-methylbutyl)-4-amino-1,2,4-triazolium ethyl sulphate	11.2 2.8	70 20	80 20	90 30	20 10	80 60	80 30	80 40
1-methyl-3,5-di cyclopentyl-4-amino-1,2,4-triazolium methyl sulphate	11.2 2.8	20 0	5 0	30 10	0 0	60 40	30 10	30 10
1-methyl-3,5-di(3-cyclohexen-1-yl)-4-methylamino-1,2,4-triazolium methyl sulphate	11.2 2.8	20 10	70 40	60 20	40 20	80 60	60 20	60 20

Examples 128—135.

- The potentiating effect of surface active agents was tested as follows. Wild oat (*Avena fatua*) seeds were sown in 10 cm pots containing sterilised loam in a greenhouse. When the plants had grown to the 2½—3 leaf stage, they were sprayed at 200 litres per hectare with an aqueous spray containing the compound 1-ethyl-3,5-diphenyl-4-methylamino-1,2,4-triazolium ethyl sulphate such that 1 or 2 kg of its cation were applied per hectare. Analogous sprays were applied containing, besides the compounds, the following surface active agents:
- | | | | |
|----|---|--|----|
| 5 | Lissapol N, | 25% of nonyl phenol condensed with 8 moles of ethylene oxide; | 5 |
| 10 | Tergitol TMN, X—77, | trimethyl nonanol condensed with 6 moles of ethylene oxide; alkyl aryl polyoxyethylene glycol plus free fatty acids in isopropanol; | 10 |
| 15 | Genapol XO80, Sapogenat T110, Tergitol NPX, Pluronic L61, | isotridecyl alcohol condensed with 8 moles of ethylene oxide; tributyl phenol condensed with 11 moles of ethylene oxide; nonyl phenol condensed with 10½ moles of ethylene oxide; or ethylene oxide — propylene oxide block copolymer containing 10% by weight ethylene oxide units, molecular weight 2,000. | 15 |
| 20 | The amount of the surface active agent in the spray volume was 0.5 or 1% except for Tergitol TMN, where the content was 0.1 or 0.5%. Three replicates were carried out for each treatment. The plants were assessed visually for percentage chemical effect/growth reduction compared with control plants 1½, 3, 5, 7 and 9 weeks after treatment. The mean results are shown in the following Table: | | 20 |

Weeks after treatment	1½		3		5		7		9	
	1	2	1	2	1	2	1	2	1	2
Rate, kg cation/ha	0.5	1	0.5	1	0.5	1	0.5	1	0.5	1
Wetting Agent, % *	20	25	40	47	58	66	71	73	79	77
Lissapol N	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5	0.1	0.5
%	10	15	15	40	45	59	64	53	60	64
Tergitol TMN	10	20	15	25	59	63	67	74	71	60
X-77	10	40	50	35	59	73	74	71	60	75
Genapol XO80	20	25	25	35	61	64	57	76	65	68
Sapogenat T110	15	15	15	50	53	58	54	67	68	70
Tergitol NPX	7	10	20	20	39	49	58	67	54	61
Pluronic L61										

* Except where stated.

Examples 136—143.

Safety to Maris Huntsman winter wheat (*Triticum vulgare*) was assessed in tests analogous to those described in Examples 75—82 except that assessment was 14, 3, 5 and 7 weeks after treatment, this winter wheat being the plant tested in the treatments being carried out at the 2 leaf stage. For comparison, difenzoquat was also tested, applying 1 or 2 kg per hectare of its cation, the material being employed as the aqueous solution of the methyl sulphate containing 250 g of cation per litre sold under the name Avenge 250 W.

The mean percentage growth reduction/chemical effect is shown in the following Table:

5

10

Weeks after Treatment		1½						3			
Chemical		Present Compound			Difenzoquat			Present Compound			Difenzoquat
Rate, kg cation/ha		1		2	1	2		1	2	1	2
Wetting Agent added, %*		0.5	1	0.5	1	—	—	0.5	1	0.5	1
Lissapol N		2	10	8	15			12	14	12	15
%		0.1	0.5	0.1	0.5			0.1	0.5	0.1	0.5
		0	0	5	10			3	8	11	13
Tergitol TMN		7	0	10	10			6	8	16	20
X-77		7	7	10	5			8	11	8	11
Genapol XO80		4	4	5	15			8	11	17	28
Sapogenat T110		3	1	5	7			4	7	11	15
Tergitol NPX		4	0	0	2			8	12	10	12
Pluronic L61			0	1					2	3	
None						20	30				28
											42

* except where stated

Weeks after Treatment	5						7					
	Present Compound			Difenzoquat			Present Compound			Difenzoquat		
	1	2		1	2		1	2		1	2	
Rate, kg cation/ha	1											
Wetting Agent added, %*	0.5	1	0.5	1	--		0.5	1	0.5	1	--	
Lissapol N	8	10	11	15			5	10	10	16		
%	0.1	0.5	0.1	0.5			0.1	0.5	0.1	0.5		
	4	10	10	12			8	11	6	13		
Tergitol TMN	3	9	14	17			8	11	14	20		
X-77	8	12	11	14			9	10	9	12		
Genapol XO80	11	14	14	27			11	12	15	20		
Sapogenat T110	7	9	7	11			8	9	10	13		
Tergitol NPX	8	14	11	14			9	15	8	12		
Pluronic L61	0			0	35	47	0		0		37	43
None												

* except where stated

It can be seen that the present compound, 1-ethyl-3,5-diphenyl-4-methylamino-1,2,4-triazolium ethyl sulphate, is much safer than difenzoquat to Maris Huntsman wheat.

Example 144.

- 5 1,4-Dimethyl-3,5-diphenyl-1,2,4-triazolium methyl sulphate 5
 (a) 3,5-Diphenyl-1-methyl-1,2,4-triazole
 10 23.6 g of 4-amino-3,5-diphenyl-1,2,4-triazole was heated at 200°C for 10
 minutes with 12.6 g of dimethyl sulphate. The resulting hot oil was dissolved in 70
 ml of 5% hydrochloric acid. The solution was cooled to 5°C and a 10% solution of 10
 sodium nitrite added dropwise with stirring, keeping the temperature at 5°C. This
 was continued until the mixture gave a positive colour with starch iodide paper.
 The sticky mixture was neutralised with 40% sodium hydroxide solution and
 extracted with 3 × 150 ml of ether. The combined ether solutions were dried over
 magnesium sulphate and evaporated down to a solid. This was then recrystallised 15
 from 500 ml of 40—60°C petroleum ether to yield 11.4 g (48%) of 3,5-diphenyl-1-
 methyl-1,2,4-triazole, m.p. 80—84°C.
 (b) 1,4-Dimethyl-3,5-diphenyl-1,2,4-triazolium methyl sulphate
 4.7 g of 3,5-diphenyl-1-methyl-1,2,4-triazole and 2.5 g of dimethyl sulphate
 were heated together at 160—170°C for 20 minutes. The product was poured out 20
 hot and when cooled it solidified to a solid which was washed with ether and dried
 to give 6.6 g (92%) of 1,4-dimethyl-3,5-diphenyl-1,2,4-triazolium methyl sulphate,
 m.p. 42—48°C.

	Analysis:	C	H	N	
	Calculated	56.46	5.30	11.62%	
25	Found	56.31	5.45	11.23%	25

The following compounds were prepared by analogous techniques.

Example 145.

1,4-Dimethyl-3,5-di-(p-tolyl)-1,2,4-triazolium methyl sulphate, m.p. 53°C.

	Analysis	C	H	N	
30	Calculated	58.59	5.95	10.79%	30
	Found	58.09	5.80	10.62%	

Example 146.

3,5-Di-(p-chlorophenyl)-1-ethyl-4-methyl-1,2,4-triazolium methyl sulphate.

	Analysis:	C	H	N	
35	Calculated	48.65	4.31	9.46%	35
	Found	48.37	4.42	9.45%	

Example 147.

3,5-Diphenyl-1-ethyl-4-methyl-1,2,4-triazolium methyl sulphate.

	Analysis	C	H	N	
40	Calculated	57.58	5.64	11.19%	40
	Found	57.25	5.75	11.22%	

Example 148.

3,5-Di-(*m*-tolyl)-1,4-dimethyl-1,2,4-triazolium methyl sulphate.

	Analysis:	C	H	N
	Calculated	58.59	5.95	10.79%
5	Found	58.11	5.81	10.45%

5

Example 149.

3,5-Di-(*m*-tolyl)-4-ethyl-1-methyl-1,2,4-triazolium methyl sulphate.

	Analysis:	C	H	N
	Calculated	60.41	6.52	10.06%
10	Found	59.92	6.25	10.20%

10

Example 150.

1,3-Diphenyl-4,5-diethyl-1,2,4-triazolium ethyl sulphate.

	Analysis:	C	H	N
	Calculated	59.93	6.24	10.41%
15	Found	59.21	6.42	10.45%

15

Example 151.

1,3-Diphenyl-5-ethyl-4-methyl-1,2,4-triazolium methyl sulphate, m.p. 120°C.

	Analysis:	C	H	N
	Calculated	57.58	5.64	11.19%
20	Found	57.54	5.88	11.47%

20

Example 152.

1,3-Diphenyl-4,5-dimethyl-1,2,4-triazolium methyl sulphate, m.p. 185—190°C.

	Analysis:	C	H	N
	Calculated	56.49	5.30	11.63%
25	Found	56.31	5.00	11.47%

25

Example 153.

1-methyl-3,4,5-triphenyl-1,2,4-triazolium methyl sulphate, m.p. 84—86°C.

	Analysis:	C	H	N
	Calculated	62.39	5.00	9.92%
30	Found	61.95	5.00	9.93%

30

Example 154.

1,3-Diphenyl-4-ethyl-5-methyl-1,2,4-triazolium ethyl sulphate, m.p. 104—106°C.

	Analysis:	C	H	N
	Calculated	58.59	5.95	10.79%
35	Found	58.51	5.60	11.05%

35

Example 155.

1-Phenyl-3-(*p*-tolyl)-4,5-dimethyl-1,2,4-triazolium ethyl sulphate.

Analysis:	C	H	N	
Calculated	57.58	5.64	11.19%	
5 Found	57.41	5.68	11.43%	5

Example 156.

1,4-dimethyl-3,5-di-*n*-pentyl-1,2,4-triazolium methylsulphate, oil.

Example 157.

1-methyl-3,5-di-*n*-pentyl-4-ethyl-1,2,4-triazolium ethylsulphate, oil.

Example 158.

- 10 Seeds of peas, mustard, linseed, ryegrass, sugarbeet, wild and cultivated oats, wheat and barley were sown in anodised aluminium pans, 19 cm long × 9.5 cm wide × 5 cm deep containing John Innes I potting compost. They were then watered and placed in a controlled environment room (22°C; 65—85% RH; 14 hours artificial illumination at 1,200 foot candles). Fourteen days after sowing the seedlings received a foliar spray of the compound of Example 144 formulated as a 50% aqueous acetone solution. The concentration of active ingredient and volume of application were adjusted so as to be equivalent to rates of 11.2 and 2.8 kg/ha in 450 litres per hectare.
- 15
- 20 After seven days growth in a controlled environment room the plants were visually assessed for any herbicidal or growth regulant response. All differences from the untreated control were scored according to a herbicidal index where 0 = no effect and 100 = complete kill.

The results are summarised in the following table:

Species	Dosage rate kg/ha	11.2	2.8
Peas — <i>Pisum sativum</i>		50	15
Mustard — <i>Sinapis alba</i>		10	5
Linseed — <i>Linum usitatissimum</i>		65	34
Ryegrass — <i>Lolium perenne</i>		5	0
Sugarbeet — <i>Beta vulgaris</i>		65	35
Oat — <i>Avena sativa</i>		70	50
Wild Oat — <i>Avena fatua</i>		70	55
Barley — <i>Hordeum vulgare</i>		5	0
Wheat — <i>Triticum aestivum</i>		10	5

Example 159.

- 30 Seeds of peas, mustard, linseed, ryegrass, sugarbeet, wild and cultivated oats, barley and wheat were sown in anodised aluminium pans, 19 cm long × 9.5 cm wide × 5 cm deep containing John Innes I potting compost. They were then watered and placed in a controlled environment room (22°C; 65—85% RH; 14 hours artificial illumination at 1,200 foot candles). Fourteen days after sowing the seedlings received a foliar spray of the compound of Example 148 formulated as a 50% aqueous acetone solution. The concentrations of active ingredient and volume of application were adjusted so as to be equivalent to rates of 11.2 and 2.8 kg/ha in 450 litres per hectare.
- 35

After seven days growth in a controlled environment room the plants were visually assessed for any herbicidal or growth regulant response. All differences

from the untreated control were scored according to a herbicidal index where 0 = no effect and 100 = complete kill.

The results are summarised in the following table:

Species	Dosage rate kg/ha	11.2	2.8
Peas — <i>Pisum sativum</i>		50	20
Mustard — <i>Sinapis alba</i>		75	50
Linseed — <i>Linum usitatissimum</i>		90	40
Ryegrass — <i>Lolium perenne</i>		75	20
Sugarbeet — <i>Beta vulgaris</i>		94	60
Oat — <i>Avena sativa</i>		80	55
Wild Oat — <i>Avena fatua</i>		80	60
Barley — <i>Hordeum vulgare</i>		20	0
Wheat — <i>Triticum aestivum</i>		15	0

5

Example 160.

5

Seeds of peas, mustard, linseed, ryegrass, sugarbeet, wild and cultivated oats, barley and wheat were sown in anodised aluminium pans, 19 cm long × 9.5 cm wide × 5 cm deep containing John Innes I potting compost. They were then watered and placed in a controlled environment room (22°C; 65—85% RH; 14 hours artificial illumination at 1,200 foot candles). Fourteen days after sowing the seedlings received a foliar spray of the compound of Example 152 formulated as a 50% aqueous acetone solution. The concentrations of active ingredient and volume of application were adjusted so as to be equivalent to rates of 11.2 and 2.8 kg/ha in 450 litres per hectare.

10

10

15

After seven days growth in a controlled environment room the plants were visually assessed for any herbicidal index where 0 = no effect and 100 = complete kill.

15

The results are summarised in the following table:

Species	Dosage rate kg/ha	11.2	2.8
Peas — <i>Pisum sativum</i>		20	5
Mustard — <i>Sinapis alba</i>		20	10
Linseed — <i>Linum usitatissimum</i>		35	10
Ryegrass — <i>Lolium perenne</i>		10	0
Sugarbeet — <i>Beta vulgaris</i>		85	60
Oat — <i>Avena sativa</i>		75	40
Wild Oat — <i>Avena fatua</i>		80	50
Barley — <i>Hordeum vulgare</i>		10	0
Wheat — <i>Triticum aestivum</i>		5	0

20

Example 161.

20

Seeds of various monocotyledon species, listed in the table below were sown in anodised aluminium pans 19 cm long × 9.5 cm wide × 5.0 cm deep, containing John

5 Innes I potting compost. They were then watered and placed in a controlled environment room (22°C; 65—85% RH; 14 hours artificial illumination at 1,600 foot candles). Fourteen days after sowing the seedlings were given a foliar spray of the compound of Example 152 formulated as aqueous acetone solution together with 1,000 ppm of the wetting agent Lissapol NX. The dosage rate was adjusted to be 2.8 kg active ingredient in 450 litres/hectare. 5

10 After a further 14 days in the controlled environment room the plants were visually assessed for any growth regulatory or herbicidal effect. All differences from an untreated control were scored on a scale 0—100 where 0 signifies no effect and 100 signifies complete suppression. 10

The results are summarised in the following table:

Species	Dosage rate kg/ha	2.8
Wheat — <i>Triticum aestivum</i>		5
Barley — <i>Hordeum vulgare</i>		5
Wild oat — <i>Avena fatua</i>		74
Blackgrass — <i>Alopecurus myosuroides</i>		34
Barnyardgrass — <i>Echinochloa crus-galli</i>		5
Crabgrass — <i>Digitaria sanguinalis</i>		50

Example 162.

15 Seeds of peas, mustard, linseed, ryegrass, sugarbeet, wild and cultivated oats, barley and wheat were sown in anodised aluminium pans, 19 cm long × 9.5 cm wide × 5 cm deep containing John Innes I potting compost. They were then watered and placed in a controlled environment room (22°C; 65—85% RH; 14 hours artificial illumination at 1,200 foot candles). Fourteen days after sowing the seedlings received a foliar spray of the compound of Example 155 formulated as a 50% aqueous acetone solution. The concentrations of active ingredient and volume of application were adjusted so as to be equivalent to rates of 11.2 and 2.8 kg/ha in 450 litres per hectare. 15

20 After seven days growth in a controlled environment room the plants were visually assessed for any herbicidal or growth regulant response. All differences from the untreated control were scored according to a herbicidal index where 0 = no effect and 100 = complete kill. 20

25 The results are summarised in the following table: 25

Species	Dosage rate kg/ha	11.2	2.8
Peas — <i>Pisum sativum</i>		75	30
Mustard — <i>Sinapis alba</i>		75	30
Linseed — <i>Linum usitatissimum</i>		95	75
Ryegrass — <i>Lolium perenne</i>		50	15
Sugarbeet — <i>Beta vulgaris</i>		85	60
Oat — <i>Avena sativa</i>		70	55
Wild Oat — <i>Avena fatua</i>		70	60
Barley — <i>Hordeum vulgare</i>		15	0
Wheat — <i>Triticum aestivum</i>		20	5

Example 163.

5 α,α' -Dichlorobenzalazine (55 parts) and unsymmetrical dimethylhydrazine (36 parts) were heated in refluxing ethanol (250 parts) for 10 hours. The solution was evaporated to dryness. The residue was then washed with water and the solid filtered off and dried to yield 4-dimethylamino-3,5-diphenyl-1,2,4-triazole (45 parts), m.p. 218°C. 5

Analysis:	C	H	N
Calculated	72.70	6.10	21.20
Found	72.63	6.25	21.37

10 On reaction with dimethyl sulphate as described in Example 1, 4-dimethylamino-1-methyl-3,5-diphenyl-1,2,4-triazolium methylsulphate, m.p. 159°C, was obtained. 10

Analysis:	C	H	N
Calculated	55.37	5.68	14.35%
Found	54.94	5.68	13.94%

15 Example 164.
4-Amino-3,5-di-*m*-tolyl-1,2,4-triazole (19.8 parts) and acetone (47.5 parts) plus 5 drops of acetic acid were heated at 200°C for 24 hours in a Carius tube. After evaporation of the excess acetone and recrystallisation from ethanol, 19.3 parts of 4-isopropylideneamino-3,5-di-*m*-tolyl-1,2,4-triazole, m.p. 143—145°C were obtained. 20

Analysis	C	H	N
Calculated	74.97	6.62	18.41%
Found	75.14	7.03	18.36%

25 This material is converted by reaction with methylsulphate and ethylsulphate respectively into the corresponding 1-methyl and 1-ethyl triazolium salts by procedures as described in Example 1. 25

Example 165.

30 3,5-Diphenyl-4-isopropylideneamino-1,2,4-triazole (17.3 parts), prepared by a method analogous to that of Example 164, was dissolved in methanol (150 parts) containing 0.3 parts of sodium. Sodium borohydride (2.9 parts) were added, and the reaction mixture was refluxed for 2 hours. After dilution with water, filtration, and recrystallisation from ethanol, 12.0 parts of 4-isopropylamine-3,5-diphenyl-1,2,4-triazole were obtained, m.p. 221—223°C. 30

35 Analysis:	C	H	N	35
Calculated	73.35	6.52	20.13%	
Found	73.47	6.61	19.88%	

40 This material is converted by reaction with methylsulphate and ethylsulphate respectively into the corresponding 1-methyl and 1-ethyl triazolium salts by procedures as described in Example 1. 40

Examples 166—192.

45 Aqueous acetone suspensions of the compounds of the Examples listed below, containing 500 ppm (wt/vol) of active ingredients together with 125 ppm of a non-ionic wetting agent were applied to the leaves of young barley plants having two fully developed leaves. The treated plants, together with controls treated only with aqueous acetone containing the wetting agent, were inoculated 24 hours after the 45

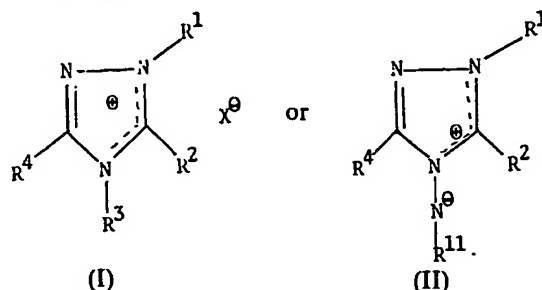
chemical application with spores of the disease organism known as barley powdery mildew, *Erisiphe graminis*. They were then placed in a water saturated atmosphere for 24 hours and 80—90% R.H.) until disease incidence was assessed 14 days later.

The % disease control for the treatments were:

5	Compound of Example No.	% Disease Control	5
	35	78	
	42	92	
	43	80	
10	44	100	10
	45	100	
	46	100	
	47	78	
	48	70	
15	49	80	15
	50	92	
	51	94	
	52	90	
	53	88	
20	54	68	20
	55	82	
	56	100	
	57	94	
	58	80	
25	59	94	25
	60	98	
	61	92	
	62	100	
	63	94	
30	64	100	30
	65	82	
	156	72	
	157	90	
	Control	0	

WHAT WE CLAIM IS:—

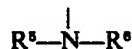
1. A method of combating pests at a locus infested or liable to be infested with them or of regulating the growth of a desired plant at a locus at which the plant is growing or is to grow, which method comprises applying to the locus a pest-combating or a plant growth regulant amount of a compound which is a 1,2,4-triazolium salt of formula



in which R¹ represents a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, aralkyl, or heterocyclic group;

R² and R⁴ are the same or different and each represents a hydrogen atom or a substituted or unsubstituted alkylthio, arylthio, or aralkylthio group or a group as defined for R¹;

R³ represents a group as defined for R¹ or the group



where R⁶ represents a hydrogen atom or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl or aryl group;

R⁵ represents a hydrogen atom; —SO₂R⁷ or



where A represents an oxygen or sulphur atom, Z represents a single bond, an oxygen or sulphur atom or an



group, R⁷ represents a substituted or unsubstituted alkyl, aryl or aralkyl group and R⁸ represents a hydrogen atom or a group as defined for R⁷; or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl or aryl group;

or R⁵ and R⁶ together represent a group of formula =CR⁹R¹⁰ where R⁹ and R¹⁰ are the same or different and each represent a hydrogen atom or a substituted or unsubstituted alkyl, aryl or aralkyl group, or R⁹ and R¹⁰ together represent an alkylene chain;

R¹¹ represents a group —SO₂R⁷ or



wherein

A, Z and R⁷ are as defined above, and X[⊖] represents one equivalent of an anion.

2. A method according to claim 1 wherein

R¹ represents an alkyl of 1—6 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, cycloalkenyl of 3—7 carbon atoms, phenyl, phenylalkyl of 7—10 carbon atoms, furyl, pyranlyl, pyrrolyl, pyridyl, quaternised pyridyl, or thienyl group, which group is

- 5 unsubstituted or substituted by one or more substituents selected from halogen, hydroxy, mercapto, alkoxy of 1—6 carbon atoms, alkylthio of 1—6 carbon atoms, alkylsulphonyl of 1—6 carbon atoms, alkylsulphinyl of 1—6 carbon atoms, alkanoyl of 1—7 carbon atoms, nitro, cyano, carboxy, esterified, salified or amidated carboxy, amino, amino substituted by 1 or 2 alkyl groups of 1—6 carbon atoms, and, except where R¹ represents substituted alkyl, alkyl of 1—6 carbon atoms; 5
- 10 R² and R⁴ are the same or different and each represents a hydrogen atom or an alkyl of 1—15 carbon atoms, alkylthio of 1—15 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, phenyl, phenylthio, phenylalkyl of 7—10 carbon atoms, phenylalkylthio of 7—10 carbon atoms, furyl, pyranlyl, pyrrolyl, pyridyl, quaternised pyridyl, or thienyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, hydroxy, mercapto, alkoxy of 1—6 carbon atoms, alkylthio of 1—6 carbon atoms, alkylsulphonyl of 1—6 carbon atoms, alkylsulphinyl of 1—6 carbon atoms, alkanoyl of 1—7 carbon atoms, nitro, carboxy, esterified, salified or amidated carboxy, amino, amino substituted by 1 or 2 alkyl groups of 1—15 carbon atoms, alkenyl or alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, and, except when it represents substituted alkyl, alkyl of 1—6 carbon atoms; 10
- 15 R³ represents a group as defined for R¹ or the group 15

- 20
$$\begin{array}{c} | \\ R^5-N-R^6 \end{array}$$
 20
- 25 where R⁶ represents a hydrogen atom or an alkyl of 1—15 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, phenylalkyl of 7—10 carbon atoms or phenyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, alkoxy of 1—6 carbon atoms, nitro and, except when R⁶ represents a substituted alkyl group, alkyl of 1—6 carbon atoms; 25
- R⁶ represents a hydrogen atom; —SO₂R⁷ or

- 30
$$\begin{array}{c} A \\ || \\ -CZR^7 \end{array}$$
 30
- where A represents an oxygen or sulphur atom, Z represents a single bond, an oxygen or sulphur atom or an

- 35
$$\begin{array}{c} | \\ -NR^8 \end{array}$$
 35
- group, R⁷ represents alkyl of 1—6 carbon atoms, phenyl or phenylalkyl of 7—10 carbon atoms and R⁸ represents a hydrogen atom or a group as defined for R⁷; or an alkyl of 1—6 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, phenylalkyl of 7—10 carbon atoms or phenyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, alkoxy of 1—6 carbon atoms, nitro and, except when R⁸ represents a substituted alkyl group, alkyl of 1—6 carbon atoms; 40
- 40 or R⁹ and R¹⁰ together represent a group of formula =CR⁹R¹⁰ where R⁹ and R¹⁰ are the same or different and each represent a hydrogen atom or an alkyl of 1—6 carbon atoms, phenyl or phenylalkyl of 7—10 carbon atoms group, which group is unsubstituted or substituted by one or more substituents selected from halogen, alkoxy of 1—6 carbon atoms, nitro and, except when it represents a substituted alkyl group, alkyl of 1—6 carbon atoms, or together represent an alkylene chain of 3—7 carbon atoms, 45
- 45 and R¹¹ represents a group —SO₂R⁷ or

- 50
$$\begin{array}{c} A \\ || \\ -CZR^7 \end{array}$$
 50
- as defined herein.
3. A method according to claim 1, wherein the compound is of formula II or of formula I where R³ represents the group



4. A method according to claim 3 wherein R¹ represents a substituted or unsubstituted alkyl, aryl or aralkyl group; and
 5 R² and R⁴ are the same or different and each represents a hydrogen atom or a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, aralkyl or alkylthio group. 5
5. A method according to claim 4 wherein R² and R⁴ are the same or different and each represents a hydrogen atom or a substituted or unsubstituted alkyl, aryl, aralkyl or alkylthio group.
- 10 6. A method according to claim 5 wherein the compound is of formula I in which R¹ represents alkyl, R² and R⁴ each represent aryl, each represent alkyl or each represent aryl monosubstituted by alkyl, R⁵ represents a hydrogen atom and R⁶ represents alkyl. 10
7. A method according to claim 1 wherein the compound is of formula I where R³ represents a group as defined for R¹. 15
8. A method according to claim 7 wherein the pests are weeds, and R¹ and R³ are the same or different and each represents a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, aralkyl or aromatic heterocyclic group. 15
9. A method according to any one of the preceding claims wherein X[⊖] represents chloride, bromide, iodide, acetate, hydroxide, sulphate, hydrogen sulphate, alkyl sulphate, *p*-toluene sulphonate, perchlorate or alkyl sulphonate. 20
10. A method according to claim 1 wherein R¹, R², R³, R⁴, R⁵, R⁶, A, Z, R⁷, R⁸, R⁹, R¹⁰ and R¹¹ have any one of the meanings they have in the compounds of formula I or II which are specified herein. 25
11. A method according to claim 10 wherein the cation of the compound is the cation of a compound of formula I or II which is specified herein. 25
12. A method according to claim 10 wherein the compound is a compound of formula I or II which is specified herein.
13. A method according to claim 1 wherein the compound is a 4-methylamino-1-ethyl-3,5-diphenyl-1,2,4-triazolium salt. 30
14. A method according to claim 1 wherein the compound is a 4-methylamino-1-ethyl-3,5-di(3-methylbutyl)-1,2,4-triazolium salt.
15. A method according to claim 1 wherein the compound is a 4-methylamino-1-ethyl-3,5-dipentyl-1,2,4-triazolium salt. 35
16. A method according to any one of claims 13—15 wherein the salt is the chloride or ethyl sulphate. 35
17. A method according to claim 1 wherein the compound is a 4-amino-1-methyl-3,5-di(3-methylbutyl)-1,2,4-triazolium salt.
18. A method according to claim 1 wherein the compound is a 4-amino-1-methyl-3,5-dipentyl-1,2,4-triazolium salt. 40
19. A method according to claim 1 wherein the compound is a 4-methylamino-1-methyl-3,5-diphenyl-1,2,4-triazolium salt.
20. A method according to claim 1 wherein the compound is a 4-methylamino-1-ethyl-3,5-di(3-methylbutyl)-1,2,4-triazolium salt. 45
21. A method according to claim 1 wherein the compound is a 4-methylamino-1-*n*-propyl-3,5-di-*n*-butyl-1,2,4-triazolium salt. 45
22. A method according to claim 1 wherein the compound is a 4-methylamino-1-*n*-pentyl-3,5-di-*n*-butyl-1,2,4-triazolium salt.
23. A method according to claim 1 wherein the compound is a 4-methylamino-1,3,5-tri-*n*-butyl-1,2,4-triazolium salt. 50
24. A method according to claim 1 wherein the compound is a 4-ethylamino-1,3,5-tri-*n*-butyl-1,2,4-triazolium salt. 50
25. A method according to claim 1 wherein the compound is a 4-ethylamino-1-(3-methylbutyl)-3,5-di-*n*-butyl-1,2,4-triazolium salt. 55
26. A method according to claim 1 wherein the compound is a 4-ethylamino-1-isobutyl-3,5-di-*n*-butyl-1,2,4-triazolium salt. 55
27. A method according to claim 1 wherein the compound is a 4-*n*-pentyl-amino-1-(3-methylbutyl)-3,5-diethyl-1,2,4-triazolium salt.
28. A method according to claim 1 wherein the compound is a 4-methylamino-1-allyl-3,5-di(3-methylbutyl)-1,2,4-triazolium salt. 60
29. A method according to claim 1 wherein the compound is a 4-*n*-propyl-amino-1-*n*-hexyl-3,5-diethyl-1,2,4-triazolium salt.

30. A method according to claim 1 wherein the compound is a 4-*n*-pentylamino-1-*n*-butyl-3,5-diethyl-1,2,4-triazolium salt.

31. A method according to any one of claims 17—30 wherein the salt is the chloride, bromide or methyl sulphate.

5 32. A method according to any one of the preceding claims wherein weeds are selectively combated in a crop. 5

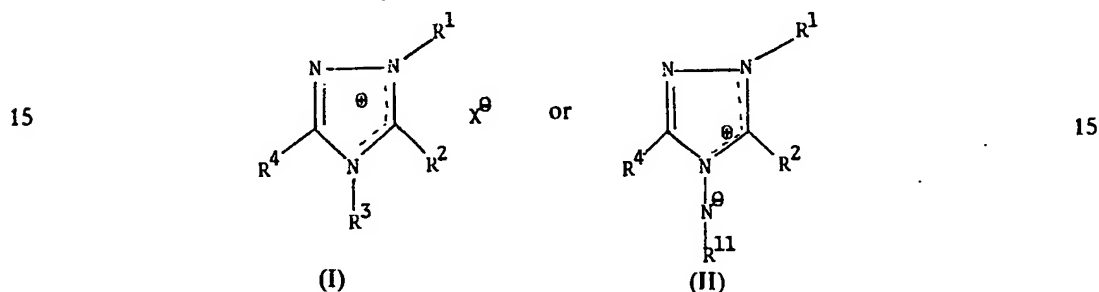
33. A method according to claim 32 wherein the crop is a cereal crop.

34. A method according to claim 32 or 33 wherein 0.5—10 kg of the compound are applied per hectare.

10 35. A method according to claim 1 performed substantially as hereinbefore described. 10

36. A method according to claim 1 performed substantially as hereinbefore described in any one of Examples 67 to 143, 158 to 162 and 166—192.

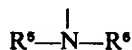
37. A compound of formula



in which R¹ represents a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aralkyl, or heterocyclic group;

20 R² and R⁴ are the same or different and each represents a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, aralkyl, alkylthio of more than 1 carbon atom, arylthio, aralkylthio or heterocyclic group; with the proviso that R² and R⁴ do not both represent methyl; 20

R³ represents the group



25 where R⁶ represents a hydrogen atom or a substituted or unsubstituted alkyl or aralkyl group; 25

R⁵ represents a hydrogen atom; —SO₂R⁷ or



where A represent an oxygen or sulphur atom, Z represents a single bond, an oxygen or sulphur atom or an



group, R⁷ represents a substituted or unsubstituted alkyl, aryl or aralkyl group and R⁸ represents a hydrogen atom or a group as defined for R⁷; or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl or aryl group;

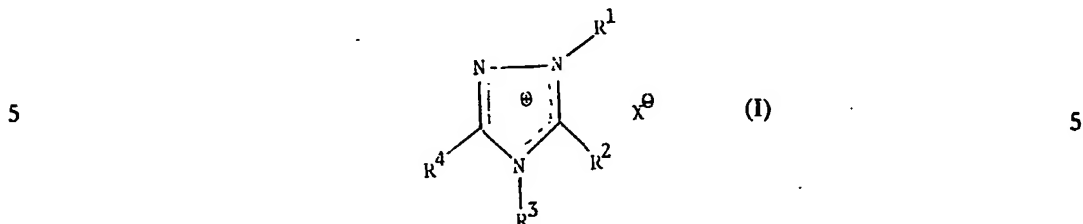
35 or R⁵ and R⁶ together represent a group of formula =CR⁹R¹⁰ where R⁹ and R¹⁰ are the same or different and each represent a hydrogen atom or a substituted or unsubstituted alkyl, aryl or aralkyl group, or R⁹ and R¹⁰ together represent an alkylene chain; 35

R¹¹ represents a group —SO₂R⁷ or



X^{\ominus} represents one equivalent of an anion; with the proviso that when R^1 represents methyl, R^2 and R^4 represent phenyl and X^{\ominus} represents bromide or iodide, then R^3 does not represent amino.

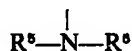
38. A compound of formula



in which R^1 represent a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, aralkyl or heterocyclic group;

R^2 and R^4 are the same or different and each represents a hydrogen atom or a substituted or unsubstituted alkylthio, arylthio, or aralkylthio group, or a group as defined for R^1 ;

R^3 represents a group



where R^5 represents a hydrogen atom or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl or aryl group;

R^6 represents a hydrogen atom; $-\text{SO}_2R^7$ or



where A represents an oxygen or sulphur atom, Z represents a single bond, an oxygen or sulphur atom or an



group, R^7 represents a substituted or unsubstituted alkyl, aryl or aralkyl group and R^8 represents a hydrogen atom or a group as defined for R^7 ; or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl or aryl group;

or R^5 and R^6 together represent a group of formula $=\text{CR}^9R^{10}$ where R^9 and R^{10} are the same or different and each represent a hydrogen atom or a substituted or unsubstituted alkyl, aryl or aralkyl group, or R^5 and R^{10} together represent an alkylene chain;

and X^{\ominus} represents alkyl sulphate, with the exception of that compound wherein X^{\ominus} represents methyl sulphate, R^1 represents methyl, R^2 and R^4 each represent a hydrogen atom and R^5 and R^6 together represent

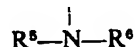


39. A compound according to claim 37 wherein

R^1 represents an alkyl of 1—6 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, cycloalkenyl of 3—7 carbon atoms, phenyl, phenylalkyl of 7—10 carbon atoms, furyl, pyranlyl, pyrrolyl, pyridyl, quaternised pyridyl, or thienyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, hydroxy, mercapto, alkoxy of 1—6 carbon atoms, alkylthio of 1—6 carbon atoms, alkylsulphonyl of 1—6 carbon atoms, alkylsulphinyl of 1—6 carbon atoms, alkanoyl of 1—7 carbon atoms, nitro, cyano, carboxy, esterified, salified or amidated carboxy, amino, amino substituted by 1 or 2 alkyl groups of 1—6 carbon atoms, and, except where R^1 represents substituted alkyl, alkyl of 1—6 carbon atoms;

R^2 and R^4 are the same or different and each represents an alkyl of 1—15

carbon atoms, alkylthio of 2—15 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, phenyl, phenylthio, phenylalkyl of 7—10 carbon atoms, phenylalkylthio of 7—10 carbon atoms, furyl, pyranyl, pyrrolyl, pyridyl, quaternised pyridyl, or thienyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, hydroxy, mercapto, alkoxy of 1—6 carbon atoms, alkylthio of 1—6 carbon atoms, alkylsulphonyl of 1—6 carbon atoms, alkanoyl of 1—7 carbon atoms, nitro, cyano, carboxy, esterified, salified or amidated carboxy, amino, amino substituted by 1 or 2 alkyl groups of 1—15 carbon atoms, alkenyl or alkynyl or 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, and, except when it represents substituted alkyl, alkyl of 1—6 carbon atoms; R^3 represents the group



where R^6 represents a hydrogen atom or an alkyl of 1—15 carbon atoms, or phenylalkyl of 7—10 carbon atoms, group, which group is unsubstituted or substituted by one or more substituents selected from halogen, alkoxy of 1—6 carbon atoms, nitro and, except when R^6 represents a substituted alkyl group, alkyl of 1—6 carbon atoms; R^6 represents a hydrogen atom; $-SO_2R^7$ or



where A represents an oxygen or sulphur atom, Z represents a single bond, an oxygen or sulphur atom or an



group, R^7 represents alkyl of 1—6 carbon atoms, phenyl or phenylalkyl of 7—10 carbon atoms and R^8 represents a hydrogen atom or a group as defined for R^7 ; or an alkyl of 1—6 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, phenylalkyl of 7—10 carbon atoms or phenyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, alkoxy of 1—6 carbon atoms, nitro and, except when R^8 represents a substituted alkyl group, alkyl of 1—6 carbon atoms; or R^8 and R^9 together represent a group of formula $=CR^9R^{10}$ where R^9 and R^{10} are the same or different and each represent a hydrogen atom or an alkyl of 1—6 carbon atoms, phenyl or phenylalkyl of 7—10 carbon atoms group, which group is unsubstituted or substituted by one or more substituents selected from halogen, alkoxy of 1—6 carbon atoms, nitro and, except when it represents a substituted alkyl group, alkyl of 1—6 carbon atoms, or together represent an alkylene chain of 3—7 carbon atoms, and R^{11} represents the group $-SO_2R^7$ or



40. A compound according to claim 39 wherein R^2 and R^4 are the same or different and each represents an alkyl of 2—15 carbon atoms, alkylthio of 2—15 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, phenyl, phenylthio, phenylalkyl of 7—10 carbon atoms, phenylalkylthio of 7—10 carbon atoms, furyl, pyranyl, pyrrolyl, pyridyl, quaternised pyridyl, or thienyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, hydroxy, mercapto, alkoxy of 1—6 carbon atoms, alkylthio of 1—6 carbon atoms, alkylsulphonyl of 1—6 carbon atoms, alkylsulphiny of 1—6 carbon atoms, alkanoyl of 1—7 carbon atoms, nitro, cyano, carboxy, esterified, salified or amidated carboxy, amino, amino substituted by 1 or 2 alkyl groups of 1—15 carbon atoms, alkenyl or alkynyl of 2—6 carbon

atoms, cycloalkyl of 3—7 carbon atoms, and, except when it represents substituted alkyl, alkyl of 1—6 carbon atoms.

41. A compound according to claim 40 wherein R⁵ represents a hydrogen atom and R⁶ represents an alkyl group of 1—15 carbon atoms.

42. A compound according to claim 38 wherein

R¹ represents an alkyl of 1—6 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, cycloalkenyl of 3—7 carbon atoms, phenyl, phenylalkyl of 7—10 carbon atoms, furyl, pyranlyl, pyrrolyl, pyridyl, quaternised pyridyl, or thienyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, hydroxy, mercapto, alkoxy of 1—6 carbon atoms, alkylthio of 1—6 carbon atoms, alkylsulphonyl of 1—6 carbon atoms, alkylsulphinyl of 1—6 carbon atoms, alkanoyl of 1—7 carbon atoms, nitro, cyano, carboxy, esterified, salified or amidated carboxy, amino, amino substituted by 1 or 2 alkyl groups of 1—6 carbon atoms, and, except where R¹ represents substituted alkyl, alkyl of 1—6 carbon atoms;

R² and R⁴ are the same or different and each represents a hydrogen atom or an alkyl of 1—15 carbon atoms, alkylthio of 1—15 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, phenyl, phenylthio, phenylalkyl of 7—10 carbon atoms, phenylalkylthio of 7—10 carbon atoms, furyl, pyranlyl, pyrrolyl, pyridyl, quaternised pyridyl, or thienyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, hydroxy, mercapto, alkoxy of 1—6 carbon atoms, alkylthio of 1—6 carbon atoms, alkynylsulphonyl of 1—6 carbon atoms, alkylsulphinyl of 1—6 carbon atoms, alkanoyl of 1—7 carbon atoms, nitro, cyano, carboxy, esterified, salified or amidated carboxy, amino, amino substituted by 1 or 2 alkyl groups of 1—15 carbon atoms, alkenyl or alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, and, except when it represents substituted alkyl, alkyl of 1—6 carbon atoms;

R³ represents a hydrogen atom or an alkyl of 1—15 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, phenylalkyl of 7—10 carbon atoms or phenyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, alkoxy of 1—6 carbon atoms, nitro and, except when R³ represents a substituted alkyl group, alkyl of 1—6 carbon atoms; and

R⁵ represents a hydrogen atom; —SO₂R⁷ or



where A represents an oxygen or sulphur atom, Z represents a single bond, an oxygen or sulphur atom or an



group, R⁷ represents alkyl of 1—6 carbon atoms, phenyl or phenylalkyl of 7—10 carbon atoms and R⁸ represents a hydrogen atom or a group as defined for R⁷; or an alkyl of 1—6 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, phenylalkyl of 7—10 carbon atoms or phenyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, alkoxy of 1—6 carbon atoms, nitro and, except when R⁵ represents a substituted alkyl group, alkyl of 1—6 carbon atoms;

or R⁸ and R⁹ together represent a group of formula =CR⁹R¹⁰ where R⁹ and R¹⁰ are the same or different and each represent a hydrogen atom or an alkyl of 1—6 carbon atoms, phenyl or phenylalkyl of 7—10 carbon atoms group, which group is unsubstituted or substituted by one or more substituents selected from halogen, alkoxy of 1—6 carbon atoms, nitro and, except when it represents a substituted alkyl group, alkyl of 1—6 carbon atoms, or together represent an alkylene chain of 3—7 carbon atoms.

43. A compound according to claim 37 wherein

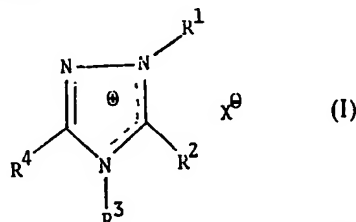
R¹ represents a substituted or unsubstituted alkyl or aralkyl group; and R² and R⁴ are the same or different and each represents a substituted or unsubstituted alkyl, alkenyl, alkynyl, aryl, cycloalkyl or cycloalkenyl group; with the proviso that R² and R⁴ do not both represent methyl.

44. A compound according to claim 43 wherein R^2 and R^4 are the same or different and each represents a substituted or unsubstituted aryl group.

45. A compound according to claim 38 wherein R^1 represents a substituted or unsubstituted alkyl, aryl or aralkyl group; and R^2 and R^4 are the same or different and each represents a hydrogen atom or a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, aralkyl or alkylthio group.

46. A compound according to claim 45 wherein R^2 and R^4 are the same or different and each represents a hydrogen atom or a substituted or unsubstituted alkyl, aryl, aralkyl or alkylthio group.

47. A compound of formula



in which R^1 represents a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aralkyl or heterocyclic group;

R^3 represents a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, aralkyl or heterocyclic group;

R^2 and R^4 are the same or different and each represents a hydrogen atom or a substituted or unsubstituted alkylthio, arylthio or aralkylthio, group, or a group as defined for R^3 ; and

X^\ominus represents one equivalent of an anion;

with the proviso that R^2 does not represent hydrogen or a substituted or unsubstituted alkyl or aryl group when R^1 represents a substituted or unsubstituted alkyl group, R^4 represents a substituted or unsubstituted alkyl or aryl group and R^3 represents a substituted or unsubstituted alkyl group and with the proviso that any phenyl group of the group R^4 is not substituted by $-\text{NO}_2$.

48. A compound according to claim 47 in which R^1 represents an alkyl of 1—6 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, cycloalkenyl of 3—7 carbon atoms, phenyl, phenylalkyl of 7—10 carbon atoms, furyl, pyranal, pyrrolyl, pyridyl, quaternised pyridyl, or thienyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, hydroxy, mercapto, alkoxy of 1—6 carbon atoms, alkylthio of 1—6 carbon atoms, alkylsulphonyl of 1—6 carbon atoms, alkanoyl of 1—7 carbon atoms, nitro, cyano, carboxy, esterified, salified or amidated carboxy, amino, amino substituted by 1 or 2 alkyl groups of 1—6 carbon atoms, and, except where it represents substituted alkyl, alkyl of 1—6 carbon atoms;

R^3 represents an alkyl of 1—6 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, cycloalkenyl of 3—7 carbon atoms, phenyl, phenylalkyl of 7—10 carbon atoms, furyl, pyranal, pyrrolyl, pyridyl, quaternised pyridyl, or thienyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, hydroxy, mercapto, alkoxy of 1—6 carbon atoms, alkylthio of 1—6 carbon atoms, alkylsulphonyl of 1—6 carbon atoms, alkylsulphinyl of 1—6 carbon atoms, alkanoyl of 1—7 carbon atoms, nitro, cyano, carboxy, esterified, salified or amidated carboxy, amino, amino substituted by 1 or 2 alkyl groups of 1—6 carbon atoms, and, except where it represents substituted alkyl, alkyl of 1—6 carbon atoms; and

R^2 and R^4 are the same or different and each represents a hydrogen atom or an alkyl of 1—15 carbon atoms, alkylthio of 1—15 carbon atoms, alkenyl of 2—6 carbon atoms, alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7 carbon atoms, phenyl, phenylthio, phenylalkyl of 7—10 carbon atoms, phenylalkylthio of 7—10 carbon atoms, furyl, pyranal, pyrrolyl, pyridyl, quaternised pyridyl, or thienyl group, which group is unsubstituted or substituted by one or more substituents selected from halogen, hydroxy, mercapto, alkoxy of 1—6 carbon atoms, alkylthio of 1—6 carbon atoms, alkylsulphonyl of 1—6 carbon atoms, alkylsulphinyl of 1—6 carbon atoms, alkanoyl of 1—7 carbon atoms, nitro, cyano, carboxy, esterified, salified or amidated carboxy, amino, amino substituted by 1 or 2 alkyl groups of 1—15 carbon atoms, alkenyl or alkynyl of 2—6 carbon atoms, cycloalkyl of 3—7

carbon atoms, and, except when it represents substituted alkyl, alkyl of 1—6 carbon atoms.

49. A compound according to claim 47 wherein R¹ represents a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aralkyl or aromatic heterocyclic group; and

R² represents a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, aralkyl or aromatic heterocyclic group.

50. A compound according to claim 37 or 47 wherein X^o represents chloride, bromide, iodide, acetate, hydroxide, sulphate, hydrogen sulphate, alkyl sulphate, *p*-toluene sulphonate, perchlorate or alkyl sulphonate.

51. A compound according to any one of claims 37, 38 and 47 wherein R¹, R², R³, R⁴, R⁵, R⁶, A, Z, R⁷, R⁸, R⁹, R¹⁰ and R¹¹ have any of the meanings they have in the compounds of formula I or II which are specified herein.

52. A compound according to any one of claims 37, 38 and 47 whose cation is specified herein.

53. A compound according to any one of claims 37, 38 and 47 which is specified herein.

54. A 4-methylamino-1-ethyl-3,5-diphenyl-1,2,4-triazolium salt.

55. A 4-methylamino-1-ethyl-3,5-di(3-methylbutyl)-1,2,4-triazolium salt.

56. A 4-methylamino-1-ethyl-3,5-dipentyl-1,2,4-triazolium salt.

57. A compound according to any one of claims 52—54 wherein the salt is the chloride or ethyl sulphate.

58. A 4-amino-1-methyl-3,5-di(3-methylbutyl)-1,2,4-triazolium salt.

59. A 4-amino-1-methyl-3,5-dipentyl-1,2,4-triazolium salt.

60. A 4-methylamino-1-methyl-3,5-dipentyl-1,2,4-triazolium salt.

61. A 4-methylamino-1-ethyl-3,5-di-(3-methylbutyl)-1,2,4-triazolium salt.

62. A 4-methylamino-1-*n*-propyl-3,5-di-*n*-butyl-1,2,4-triazolium salt.

63. A 4-methylamino-1-*n*-pentyl-3,5-di-*n*-butyl-1,2,4-triazolium salt.

64. A 4-methylamino-1,3,5-tri-*n*-butyl-1,2,4-triazolium salt.

65. 4-Methylamino-1,3,5-tri-*n*-butyl-1,2,4-triazolium bromide.

66. A 4-ethylamino-1,3,5-tri-*n*-butyl-1,2,4-triazolium salt.

67. A 4-ethylamino-1-(3-methylbutyl)-3,5-di-*n*-butyl-1,2,4-triazolium salt.

68. A 4-ethylamino-1-isobutyl-3,5-di-*n*-butyl-1,2,4-triazolium salt.

69. A 4-*n*-pentylamino-1-(3-methylbutyl)-3,5-diethyl-1,2,4-triazolium salt.

70. A 4-methylamino-1-allyl-3,5-di(3-methylbutyl)-1,2,4-triazolium salt.

71. A 4-*n*-propylamino-1-*n*-hexyl-3,5-diethyl-1,2,4-triazolium salt.

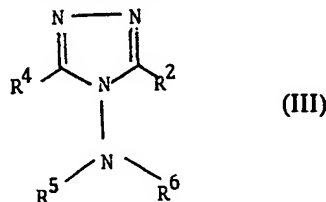
72. A 4-*n*-pentylamino-1-*n*-butyl-3,5-diethyl-1,2,4-triazolium salt.

73. A compound according to any one of claims 58—64 and 66—72 wherein the salt is the chloride, bromide or methyl sulphate.

74. A compound according to any one of claims 37, 38 and 47 substantially as hereinbefore described.

75. A compound according to any one of claims 37, 38 and 47 substantially as hereinbefore described in any one of the Examples.

76. A process for preparing a compound claimed in claim 37 or 38 which has formula I, which process comprises quaternising a 1,2,4-triazole of formula



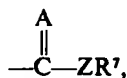
with a compound of formula R⁵X.

77. A process for preparing a compound claimed in claim 37 or 38 which has formula I wherein R⁵ and R⁶ together represent a group of formula =CR⁹R¹⁰, which process comprises reacting the corresponding compound in which R⁵ and R⁶ each represents a hydrogen atom with an aldehyde or ketone of formula R⁹COR¹⁰.

78. A process for preparing a compound claimed in claim 37 which has formula II, which process comprises reacting the corresponding compound of formula I where R⁶ represents a hydrogen atom with a base.

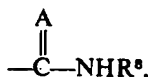
79. A process for preparing a compound claimed in claim 37 or 38 which has formula I, which process comprises reacting the corresponding compound of formula II with a compound of formula R⁶X.

80. A process for preparing a compound claimed in claim 37 or 38 which has formula I wherein R^5 represents $-\text{SO}_2R^7$ or



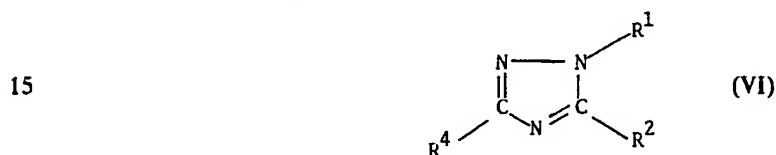
5 which process comprises reacting the corresponding compound of formula I or II in which R^5 represents a hydrogen atom with a halide or anhydride of formula R^5Y or $R^5\text{OR}^6$, where Y represents a halogen atom. 5

81. A process for preparing a compound claimed in claim 37 or 38 wherein R^5 represents



10 which process comprises reacting the corresponding compound in which R^5 represents a hydrogen atom with an isocyanate or isothiocyanate of formula $R^5\text{NCO}$ or $R^5\text{NCS}$ respectively. 10

82. A process for preparing a compound claimed in claim 47, which process comprises reacting a triazole of formula



with a compound of formula R^3X .

83. A process for preparing a compound claimed in any one of claims 37, 38 and 47, which process is substantially as hereinbefore described.

20 84. A process for preparing a compound claimed in any one of claims 37, 38 and 47, which process is substantially as hereinbefore described in any one of the Examples. 20

85. A compound claimed in any one of claims 37, 38 and 47 when prepared by a process claimed in any one of claims 76—84.

25 86. A pesticidal or plant growth regulant composition comprising a compound as defined in claim 1 together with at least one material selected from solid carriers, a liquid carrier which is a hydrocarbon which boils within the range $130-270^\circ\text{C}$, surface active agents, other pesticides, other plant growth regulants, antidotes, ammonium sulphate, fertilizers and bases. 25

30 87. A pesticidal or plant growth regulant composition comprising a compound as claimed in any one of claims 37, 38 and 47 together with at least one material selected from carriers, surface active agents, other pesticides, other plant growth regulants, antidotes, ammonium sulphate, fertilizers and bases. 30

88. A composition according to claim 86 or 87 which contains a surface active agent.

35 89. A composition according to claim 86 or 87, which composition is substantially as hereinbefore described. 35

90. A composition according to claim 86 or 87, which composition is substantially as hereinbefore described in any one of the Examples 67 to 143, 158 to 162 and 166 to 192.

40 91. A process for preparing a composition claimed in any one of claims 86—90, which process comprises admixing the ingredients. 40

92. A composition claimed in any one of claims 86—90 when prepared by a process claimed in claim 91.

93. A method according to claim 1 wherein the compound is applied in the form of a composition claimed in any one of claims 86—90 and 92.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1980.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.